

Substituent effects on tautomerization of oxepine to benzene oxide: a Hammett study via ab initio

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Received 9 June 2004; revised 9 October 2004; accepted 2 November 2004

Available online 21 December 2004

Abstract

In order to find the susceptibility of the oxepine to benzene oxide tautomerization to the substituent effects, equilibrium constants are found for conversion of 3-(X)-oxepines to their corresponding 2-(X)-benzene oxides (Series 1), as well as 4-(X)-oxepines to analogous 3-(X)-benzene oxides (Series 2) where X=H, NH₂, OCH₃, CH₃, CF₃, F, Cl, Br, NO₂ and CN. For the equilibria related to Series 1, the K_{eq} are: 31.29 (H), 0.01 (NH₂), 498.58 (OCH₃), 2.71 (CH₃), 4.19 (CF₃), 0.31 (F), 1.03 (Cl), 1.72 (Br), 0.31 (NO₂) and 1.89 (CN). For Series 2, the K_{eq} are: 31.29 (H), 47.73 (NH₂), 7.97 (OCH₃), 16.48 (CH₃), 44.61 (CF₃), 52.81 (F), 52.81 (Cl), 64.67 (Br), 374.21 (NO₂) and 107.31 (CN). Experimental K_{eq} has only been reported for X=H, which appears to consistent with that calculated in this report. Using B3LYP/6-31G* Hammett ρ value of 0.8 and 0.6 are obtained for Series 1 and 2, respectively; suggesting that electron withdrawing groups slightly shift the equilibrium in favor of benzene oxide.

All rate constants (k_p), activation electronic energies (ΔE^\ddagger), enthalpies (ΔH^\ddagger) and Gibbs free energies (ΔG^\ddagger) for $1 \rightleftharpoons 2$ tautomerizations, are calculated at HF, DFT (B3LYP) and MP2 levels of theory, using 6-31G* standard basis set.

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Keywords: Hammett; Substituent effect; Valence tautomerizations; Electronic effects; Oxepine; Benzene oxide; MP2; DFT methods

1. Introduction

The binary valence tautomerization system of oxepine (**1**) \rightleftharpoons benzene oxide (**2**) is of biological importance (Fig. 1) [1–10]. This tautomerization system is of particular interest to us and many other chemists because it is rapid, thermally allowed and a disrotatory type of electrocyclic interconversion [11–15].

NMR studies show that **1** has a boat conformation in equilibrium with its mirror image [16–18]. Preparation of **2** and a number of its derivatives are already reported [19,20]. A few studies on the rates of their valence isomerizations have appeared [21,22].

Tautomerization between **1** and **2** may be regarded as a system with fluctuating bonds. At 0 °C, this proceeds approximately 10⁴ times faster than that of bullvalene system. The rate constant for $1 \rightleftharpoons 2$ valence tautomerisation

is determined using low temperature ¹H NMR. The equilibrium position favors **1** at lower temperatures and **2** above the ambient. A dynamic NMR investigation on $1 \rightleftharpoons 2$ isomerizations is reported using a prochiral substituent. The activation parameter for the valence isomerization/degenerate racemization process is given as: $\Delta G^\ddagger = 7.6$, $\Delta H^\ddagger = 8.6$ and $\Delta S^\ddagger = 5.8$ kcal mol⁻¹ [23]. However, NMR characterizations of $1 \rightleftharpoons 2$ tautomerizations are more suitable when the equilibrium constant (K_{eq}) is less than 20 [24,25].

Theoretical determination of molecular structure and conformation, puckering of **1** and its oxanorcaradiene valence tautomer **2** is already reported [22]. This is carried out by employing STO-3G, 4-31G and 6-31G* basis sets. Again, it is found that the **1** possess a boat conformation with a constant admixture of 22% chair character, leading to a flattening of the triene part and *N*-electron delocalization, typical for a planar polyene. Up to date, little experimental and almost no theoretical reports have appeared on the susceptibility of oxepine to benzene oxide valence tautomerization systems to the electrical effects.

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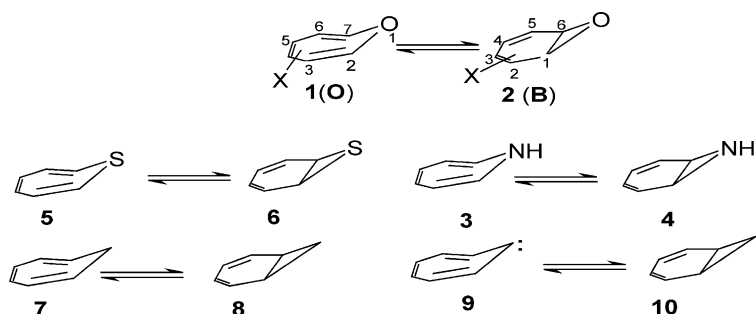


Fig. 1. Binary valence tautomerizations in seven membered ring systems.

Following up on our previous investigations, in this manuscript Hammett substituent effects on valence tautomerization in oxepine-benzene oxide system are reported using ab initio calculations.

2. Computational methods

Geometry optimizations are carried out by HF and B3LYB methods [26,27]. This is using 6-31G* basis set of the GAUSSIAN 98 system of programs [28]. Global minima are specified on corresponding energy surfaces through relax scan using Keyword 'FOPT (Z-matrix)' at HF/6-31G* level of theory. The optimized geometrical outputs of the latter are used as inputs for the B3LYB/6-31G* calculations. Single point calculations are done via MP2/6-31G*. This is for obtaining more accurate values of activation electronic energies (ΔE^\ddagger), enthalpies (ΔH^\ddagger) and Gibbs free energies (ΔG^\ddagger). In order to find energy minima keyword 'FOPT' and for transition states keyword 'FOPT (QST3)' are used. To confirm the nature of the stationary species and evaluate the activation energy barriers for valence tautomerisation, frequency calculations (keyword: FREQ=NORAMAN) are carried out. This is for ground and transition states, at both HF and DFT levels. For minimum state structures, only

real frequency values and for the transition states, only a single imaginary frequency value is accepted [27]. Thermodynamic functions obtained through frequency calculations, are multiplied by the proper scaling factors. This is to account for the difference between the harmonic vibrational calculations and the anharmonic oscillations of the actual bonds.

In order to find substituent effects on tautomerization of benzene oxide to oxepine, Hammett study via ab initio is employed in this manuscript. Originally, Hammett study was based on ionizations of *m*- and *p*-XC₆H₄Y, where 'log $k/k_0 = \rho\sigma$ ' was introduced as 'the Hammett equation' [29]. In this equation k_0 is the rate constant or equilibrium constant for X=H, k is the constant for the group X, ρ is a constant for a given reaction under a given set of conditions, and σ is a constant characteristic of the group X. Employment of B3LYP/6-31G* gives a similar Hammett ρ value compared to that obtained through HF/6-31G* for Series 2. A rather different ρ value than that obtained via HF/6-31G* is calculated by B3LYP/6-31G* for Series 1 (Fig. 2). Moreover, better correlation factors are obtained for Series 2 than Series 1. Both of these points indicate more involvement of steric effect in Series 1, compared to Series 2 (Fig. 2) [29].

3. Results and discussion

Thermodynamic data are presented for 3-(X)-oxepines to their corresponding 2-(X)-benzene oxides (Series 1), as well as 4-(X)-oxepines to analogous 3-(X)-benzene oxides (Series 2), where X=H, NH₂, OCH₃, CH₃, CF₃, F, Cl, Br, NO₂ and CN (Fig. 1, Tables 1 and 2). These are calculated at HF/6-31G*, B3LYP/6-31G* and MP2/6-31G*// HF/6-31G*, which include: sum of electronic and thermal energies (E), sum of electronic and thermal enthalpies (H), sum of electronic and thermal Gibbs free energies (G), dipole moments (μ) and exact polarizabilities (η) for the ground state of benzene oxides (B), 2, and oxepines (O), 1, as well as their corresponding transition states (TS)¹ obtained by the FREQUENCY option of the GAUSSIAN 98 program [15]. Using the above data changes of activation

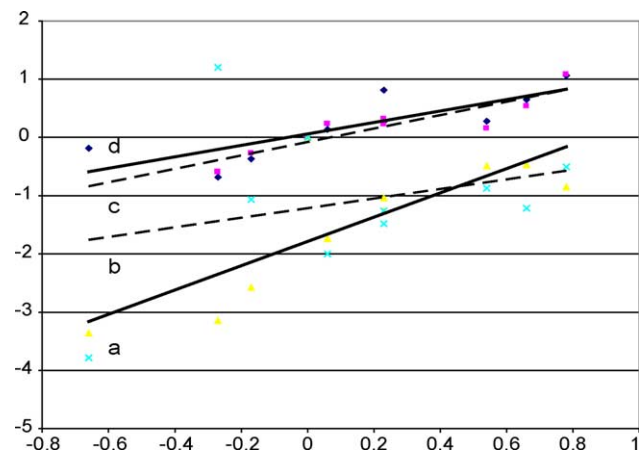


Fig. 2. Hammett ρ values obtained for oxepine-benzene oxide tautomerizations for Series 1 and 2. (a) Series 1, via HF/6-31G*: $\rho=2.08$, $R^2=0.625$. (b) Series 1, via B3LYP/6-31G*: $\rho=0.8$, $R^2=0.08$. (c) Series 2, via HF/6-31G*: $\rho=0.98$, $R^2=0.66$. (d) Series 2, via B3LYP/6-31G*: $\rho=0.63$, $R^2=0.5$.

¹ $G = H - TS = (E + RT) - TS = [(E_0 + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}) + RT] - TS$, where: $E_0 = E_{\text{elec}} + ZPE$.

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