Kinetic and thermodynamic study of substituent effect on the Claisen rearrangement of para-substituted allyl aryl ether: a Hammett study via DFT

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ABSTRACT

In order to find the susceptibility of the Claisen rearrangement and next proton shift reaction of allyl aryl ether to the substituent effects in para position, the kinetic and thermodynamic parameters are calculated at the B3LYP level using 6-311G** basis set. The calculated activation energies for the rearrangements and proton shift reactions are around 33.33 kcal/mol and 52.16 kcal/mol, respectively. Negative values for the activation entropy confirm the concerted mechanism for the Claisen rearrangement and proton shift reaction. The Hammett ρ value of -1.3433 obtained in Claisen rearrangement. Negative Hammett ρ value indicates that the electron donating groups slightly increase the rate of Claisen rearrangement. Positive Hammett ρ value (2.5132) for proton shift reaction indicates that electron withdrawing groups increase the rate of reaction.

Keywords: Hammett; Density functional theory; Substituent effect, Claisen rearrangement; Allyl aryl ether

INTRODUCTION

A typical organic reaction proceeds in a special mechanism. There maybe several proposed mechanisms for a typical organic reaction. Experimental methods have many instrumental limitations, such as trapping the intermediates or transition states (TSs) in confirming the mechanism that reactions proceed from it. Computational methods can make confirming the mechanism easer, cheaper, and exacter. For example, the gas phase kinetics and the mechanism of two retro-cheletropic ene reactions were studied by computational methods, therefore, the stepwise mechanism was rejected and the concerted mechanism was fully investigated [1]. Among the most efficient reactions in terms of atom economy are the [3, 3] sigmatropic shifts, that allow the formation of a C–C bond through the rearrangement of the molecule [2]. The [3,3] sigmatropic rearrangement of allyl vinyl ethers,

which allows the preparation of γ,δ-unsaturated carbonyl compounds, is worthy of study due to its special synthetic relevance as well as the large number of theoretical studies generated. This reaction, first reported by Ludwig Claisen in 1912, [3] was originally described as "the thermal isomerization of an allyl vinyl ether or of its nitrogen or sulfur containing analogue derivativessto afford a bifunctionalized molecule in a $[\pi^2s + \sigma^2s + \pi^2s]$ process.

The development of the aliphatic Claisen rearrangement was simultaneous with the study of the aromatic version of the reaction [4, 5, 6]. Thus, in the Claisen rearrangement of an allyl aryl ether, the first [3, 3] step affords an ortho dienone which usually enolizes into an o-allylphenol. It is the reaction known as the ortho Claisen rearrangement (Scheme 1).
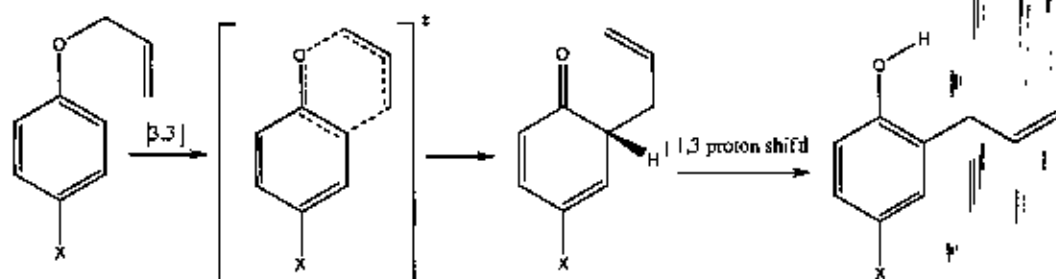
Scheme 1. Claisen rearrangement of allyl aryl ether and 1,3-proton shift of intermediate. X=H, NO$_2$, CN, CHO, F, Cl, NH$_2$, NHCH$_3$, OH, OCH$_3$, CH3.

Table 1. Hammett substituent constant values [9]

X	σ_p
H	0
NO$_2$	0.780
CN	0.650
CHO	0.450
F	0.060
Cl	0.220
NH$_2$	- 0.630
NHCH$_3$	- 0.840
OH	- 0.380
OCH$_3$	- 0.280
CH$_3$	- 0.170

In the present work we extended our studies to discover the effect of substituent in the rearrangement and 1,3-proton shift reaction of allyl aryl ether by applying the Hammett equation. Eq. (1) shows the basic form of the Hammett equation [7]:

$$\log\frac{k_X}{k_H} = \rho\sigma \qquad (1)$$

in which k_X is the rate constant for a side chain reaction of a benzene derivative where a substituent is in para or meta position with respect to the side chain and k_H is the corresponding quantity for the unsubstituted compound; σ is a Hammett substituent constant which in principle is characteristic of the substituent, and ρ is a reaction constant, which depends on the nature of the reaction. The Hammett equation is an of the important example of linear free energy relationships (LFERs), which widely used in studies of the chemical reactivity of substituted benzenes [8]. Several compilations of the Hammett σ_p and enhanced σ_p (σ^-) values [9] are tabulated in Table 1.

COMPUTATIONAL DETAILS

The structures corresponding to the reactants, TSs, intermediates, and products (Scheme 1) were optimized, using the Gaussian 03 computational package [10] with DFT method. The optimized geometries of the stationary points on the potential energy surfaces (PES) were performed using the Becke's three-parameter hybrid exchange functiooal with the correlation functional of Lee, Yang, and Parr (B3LYP) [11,12] with the 6-311G** basis set. To confirm the nature of the stationary species and evaluate the activation energy barriers, frequency calculations are carried out. For minimum state structures, only real frequency values and for the transition states, only a single imaginary frequency value is accepted. The synchronous transit guided quasi-Newton (STQN) method [13] was used to locate the TSs. The activation energies, E_a and the Arrhenius factors were computed using Eqs. (2) and (3), respectively, which were derived from the transition state theory [14,15]:

$$E_a=\Delta H^{\neq}(T)+RT \qquad (2)$$
$$A=(ek_B T/h) \exp(\Delta S^{\neq}(T)/R) \qquad (3)$$

Thermodynamic parameters were calculated at 298.15 K and 1.0 atm.

RESULTS AND DISCUSSION

Thermodynamic data are presented for allyl aryl ether to their corresponding intermediates (sigmatropic reaction), and for intermediates to corresponding ortho-allylphenols (1,3-proton shift), with different substituent (Scheme 1, Table 2). These are calculated at the B3LYP/6-311G** level, which include: sum of electronic and thermal enthalpies (H), sum of electronic and thermal Gibbs free energies (G), and entropies (S) for the ground state of reactants, products, intermediates, and their corresponding transition states (TS). Using the above data, the equilibrium constants (K_{eq}), Gibbs free energies (ΔG°), enthalpies (ΔH°), and entropies (ΔS°) of reactions for both rearrangement and 1,3-proton shift reaction are calculated and collected in Table 3. The activation energies (E_a), rate constants (k), pre exponential factors (A), enthalpies of activation ($\Delta H^{\neq}$), Gibbs activation free energies ($\Delta G^{\neq}$), activation entropies ($\Delta S^{\neq}$), n_T (the position of the transition structure along the reaction coordinate), and $\log(k_v/k_{11})$ for sigmatropic rearraagements and 1,3-proton shift reactions, are presented in Tables 4 and 5.

Table 2. Calculated B3LYP/6-311G** thermodynamic data for Claisen rearrangement and next proton shift reaction including: sum of electronic and thermal Gibbs free energies (G), sum of electronic and thermal enthalpies (H), and entropies (S) for the ground state of reactants (R), product (P). intermediates (IM). and their corresponding transition states (TS1 and TS2)

Substituent	State	G (Hartree)	H (Hartree)	S (cal/mol.K)
	R	-424.144449	-424.099781	94.012
	TS1	-424.088993	-424.046494	89.446
H	IM	-424.127028	-424.081623	95.562
	TS2	-424.045102	-424.000720	93.410
	P	-424.161432	-424.117279	92.927
	R	-628.704962	-628.653486	108.341
	TS1	-628.648739	-628.599225	104.211
NO$_2$	IM	-628.683430	-628.630914	110.529
	TS2	-628.604420	-628.553326	107.536
	P	-628.722172	-628.671414	106.830
	R	-516.414913	-516.365942	103.069
	TS1	-516 359004	-516 311848	99.249
CN	IM	-516.393469	-516.343615	104.926
	TS2	-516.314180	-516.265267	102.945
	P	-516.432037	-516.383637	101.867
	R	-537.494920	-537.445442	104.135
	TS1	-537.439466	-537.391952	100.002
CHO	IM	-537.475974	-537.425604	106.011
	TS2	-537.396362	-537.347134	103.609
	P	-537.511842	-537.462994	102.810
	R	-523.416821	-523.369989	98.565
	TS1	-523.362086	-523.317417	94.015
F	IM	-523.399361	-523 351769	100.166
	TS2	-523.315284	-523.268783	97.869
	P	-523.433706	-523.387443	97.369

Table 2. Continued…

Substituent	State	G (Hartree)	H (Hartree)	S (cal/mol.K)
	R	-883.777636	-883.729594	101.114
	TS1	-883.722605	-883.676578	96.872
Cl	IM	-883.759367	-883.710532	102.782
	TS2	-883.676554	-883.628707	100.703
	P	-883.794519	-883.747096	99.810
	R	-479.499842	-479.451814	101.084
	TS1	-479.447232	-479.401320	96.630
NH₂	IM	-479.483971	-479.435389	102.248
	TS2	-479.398025	-479.350359	100.322
	P	-479.516427	-479.468966	99.889
	R	-518.788849	-518.737429	108.223
	TS1	-518.737738	-518.688238	104.182
NHCH₃	IM	-518.774855	-518.722923	109.300
	TS2	-518.687727	-518.636981	106.804
	P	-518.805341	-518.754517	106.969
	R	-499.382736	-499.335224	99.998
	TS1	-499.329468	-499.284262	95.144
OH	IM	-499.367419	-499.319381	101.104
	TS2	-499.281683	-499.234550	99.200
	P	-499.399283	-499.352299	98.886
	R	-538.666838	-538.616011	106.974
	TS1	-538.614446	-538.565839	102.302
OCH₃	IM	-538.653173	-538.601806	108.112
	TS2	-538.566712	-538.516402	105.886
	P	-538.683275	-538.633010	105.792
	R	-463.447386	-463.397660	104.659
	TS1	-463.391771	-463.345324	97.757
CH₃	IM	-463.430263	-463.381163	103.339
	TS2	-463.346738	-463.298407	101.722
	P	-463.463962	-463.414957	103.140

Kinetic and thermodynamic study

Calculations show that the sigmatropic rearrangements with various substituents are endothermic ($\Delta H^{\circ} > 0$) and the global rearrangement process is aot spontaneous ($\Delta G^{\circ} > 0$), on the other hand the proton shift reactions with all studied substituents are exothermic ($\Delta H^{\circ} < 0$) and the global proton shift reactions are spontaneous ($\Delta G^{\circ} < 0$). Our calculated ΔG° for the sigmatropic rearrangements and proton shift reactions are very similar to their numerically calculated values of ΔH° (Table 3). As we can see from Table 3, the calculated entropy values are generally small (absolute values of ΔS° are less than 2.2 cal/mol.K for the rearrangements and 3.7 cal/mol.K for the proton shift reactions). These results indicate that the entropy effect on the Gibbs free energy is very small and the entropy term and $T\Delta S^{\circ}$ value can be neglected for the equilibria constant. Thus, the enthalpic term is dominant in the determinatioa of the equilibrium constant. From Tables 4 and 5 we can see that the calculated Gibbs free energy barriers for the sigmatropic rearrangements and proton shift reactions with various substituents are on average 34.08 kcal/mol and 52.22 kcal/mol, respectively, which are very similar to the calculated enthalpy barriers. Activation energies for the rearrangements and proton shift reactions are around 33.33 kcal/mol and 52.16 kcal/mol, respectively. The normal range for the experimental activation energies of Claisen rearrangemeot with methyl substituent in para position is about 36.08 kcal/mol [1].

Table 3. Changes of thermal Gibbs free energies ($\Delta G^\cdot$), thermal enthalpies ($\Delta H^\cdot$), entropies ($\Delta S^\cdot$), and equilibrium constants (K_{eq}) Calculated at B3LYP/6-311G** level of theory for Claisen rearrangement and next proton shift reaction

Substituent	Rearrangement				Proton shift			
	$\Delta G^\cdot$ (kcal/mol)	$\Delta H^\cdot$ (kcal/mol)	$\Delta S^\cdot$ (cal/mol K)	K_{eq}	$\Delta G^\cdot$ (kcal/mol)	$\Delta H^\cdot$ (kcal/mol)	$\Delta S^\cdot$ (cal/mol.K)	K_{eq}
H	10.931	11.394	1.550	9.677×10^{-9}	-21.588	-22.374	-2.635	6.714×10^{15}
NO$_2$	13.511	14.164	2.188	1.243×10^{-10}	-24.278	-25.414	-3.699	6.298×10^{17}
CN	13.456	14.810	1.857	1.364×10^{-10}	-24.281	-25.114	-3.859	5.528×10^{17}
CHO	11.888	12.448	1.876	1.923×10^{-9}	-22.587	-23.462	-3.281	3.1658×10^{16}
F	10.956	11.433	1.601	9.285×10^{-9}	-21.551	-22.385	-2.797	6.307×10^{15}
Cl	11.463	11.961	1.668	3.941×10^{-9}	-22.058	-22.944	-2.972	1.482×10^{16}
NH$_2$	9.959	10.306	1.164	4.998×10^{-8}	-20.366	-21.069	-2.359	8.528×10^{14}
NHCH$_3$	8.781	9.102	1.877	3.649×10^{-7}	-19.130	-19.825	-2.331	1.057×10^{14}
OH	9.611	9.941	1.106	8.987×10^{-8}	-19.994	-20.656	-2.218	4.555×10^{14}
OCH$_3$	8.574	8.913	1.138	5.171×10^{-7}	-18.889	-19.588	-2.320	7.046×10^{13}
CH$_3$	10.744	10.352	-1.328	1.326×10^{-8}	-21.146	-21.206	-0.199	3.181×10^{15}

Table 4. Activation parameters, position of the transition structures and $\log(k_X/k_H)$, calculated at the B3LYP/6-311G** level of theory for Claisen rearrangement

Substituent	ΔG^z (kcal/mol)	ΔH^z (kcal/mol)	ΔS^z (cal/mol.K)	n_T	E_a (kcal/mol)	logA	k (S^{-1})	$\log(k_X/k_H)$
H	34.799	33.438	-4.566	8.593	34.030	12.229	1.910×10^{-13}	0.000
NO$_2$	35.280	34.049	-4.138	0.618	34.641	12.324	8.484×10^{-14}	-0.352
CN	35.083	33.944	-3.820	8.618	34.536	12.392	1.183×10^{-13}	-0.208
CHO	34.797	33.565	-4.133	0.603	34.157	12.323	1.914×10^{-13}	0.0009
F	34.346	32.989	-4.550	8.594	33.581	12.231	4.099×10^{-13}	8.331
Cl	34.532	33.268	-4.232	0.599	33.860	12.299	2.996×10^{-13}	0.195
NH$_2$	33.013	31.685	-4.454	0.588	32.277	12.253	3.893×10^{-12}	1.309
NHCH$_3$	32.072	38.867	-4.841	0.579	31.460	12.344	1.907×10^{-11}	1.999
OH	33.426	31.979	-4.854	0.583	32.571	12.166	1.939×10^{-12}	1.006
OCH$_3$	32.876	31.483	-4.672	0.574	32.875	12.205	4.905×10^{-12}	1.409
CH$_3$	34.898	32.841	-6.902	0.590	33.433	11.717	1.614×10^{-13}	-0.073

Table 5. Activation parameters, position of the transition structures and $\log(k_X/k_H)$, calculated at the B3LYP/6-311G** level of theory for proton shift reaction

Substituent	ΔG^z (kcal/mol)	ΔH^z (kcal/mol)	ΔS^z (cal/mol.K)	n_T	E_a (kcal/mol)	logA	k (S^{-1})	$\log(k_X/k_H)$
H	51.409	50.767	-2.152	8.413	51.359	12.756	1.270×10^{-25}	0.000
NO$_2$	49.579	48.687	-2.993	0.481	49.279	12.572	2.789×10^{-24}	1.341
CN	49.754	49.164	-1.981	0.482	49.756	12.794	2.075×10^{-24}	1.213
CHO	49.957	49.240	-2.402	0.408	49.833	12.701	1.474×10^{-24}	1.064
F	52.759	52.074	-2.297	0.415	52.666	12.724	1.301×10^{-26}	-0.989
Cl	51.965	51.346	-2.879	0.412	51.938	12.772	4.965×10^{-26}	-0.407
NH$_2$	53.931	53.357	-1.926	8.420	53.949	12.885	1.797×10^{-27}	-1.849
NHCH$_3$	54.673	53.929	-2.496	8.425	54.521	12.681	5.139×10^{-28}	-2.392
OH	53.800	53.232	-1.904	0.421	53.824	12.818	2.245×10^{-27}	-1.752
OCH$_3$	54.255	53.591	-2.226	0.425	54.184	12.740	1.841×10^{-27}	-2.086
CH$_3$	52.412	51.930	-1.617	0.416	52.522	12.873	2.335×10^{-26}	-0.735

Position of the transition structures

Hammond's postulate can be interpreted in terms of the position of the transition structure along the reaction coordinate, n_T, (Eq.4) as defined by Agmon [16]:

$$n_T = \frac{1}{2-(\Delta G^o/\Delta G^{\neq})} \qquad (4)$$

According to this equation, the position of the transition state along the reaction coordinate is determined solely by $\Delta G^{\cdot}$ (a thermodynamic quantity) and $\Delta G^{\neq}$ (a kinetic quantity). According to Table 4, the values of n_T for the Claisen rearrangement with various substutuent are >0.5 but for the proton shift reaction with various substutuents these values are <0.5. The magnitudes of n_T, that indicate the degree of similarity between the transition structure and the product, for the rearrangement with electron withdraw substituent are greater than with electron donor substituent, but for the proton shift reaction this conclusion is reversed. This sequence implies that among the transition structures, those in the rearrangement have the largest similarity to the product and in the proton shift reaction have the smaller resemblance to the product.

Hammett study

Plots of $\log(k_X/k_H)$ (Tables 4 and 5) vs. Hammett substituent constant for the rearrangement and proton shift reactions are shown in Figs. 1-2. The results of a linear regression for $\log(k_X/k_H)$ versus Hammett σ constant for the rearrangement and proton shift reaction are given in Eqs. 5 and 6:

$$\log\left(\frac{k_X}{k_H}\right)_{Rearrangement} = -1.3433\sigma_p + 0.4935 \quad R^2 = 0.7728 \quad (5$$

$$\log\left(\frac{k_X}{k_H}\right)_{Proton\ shift} = 2.5132\sigma_p - 0.5673 \quad R^2 = 0.8911 \qquad (6$$

The Hammett ρ value of -1.3433 (Fig.1) is obtained for Claisen rearrangement and the correlation coefficient between $\log(k_X/k_H)$ and σ_p is 0.7728 (Fig.2). Negative Hammett ρ value indicates that the electron donating groups moderately increase the rate of Claisen rearrangement. Positive Hammett ρ value (2.5132) for proton shift reaction indicates that the electron withdrawing groups increase the rate of reaction.

CONCLUSION

DFT calculations portray a clear picture of electronic effect on allyl aryl ether rearrangement and its next step (proton shift reaction).The agreement between the numerical values of $\log(k_X/k_H)$ and Hammett substituent constant were excellent and Eqs. 5 and 6 describe these relationships. Negative Hammett ρ value for Claisen rearrangement indicates that the electron donating groups moderately increase the rate of the reaction; on the other hand positive value indicates that the electron withdrawing groups increase the proton shift reaction rate. Considerable deviation of the correlation factor from 1 indicates that the steric parameters could be important in these reactions.
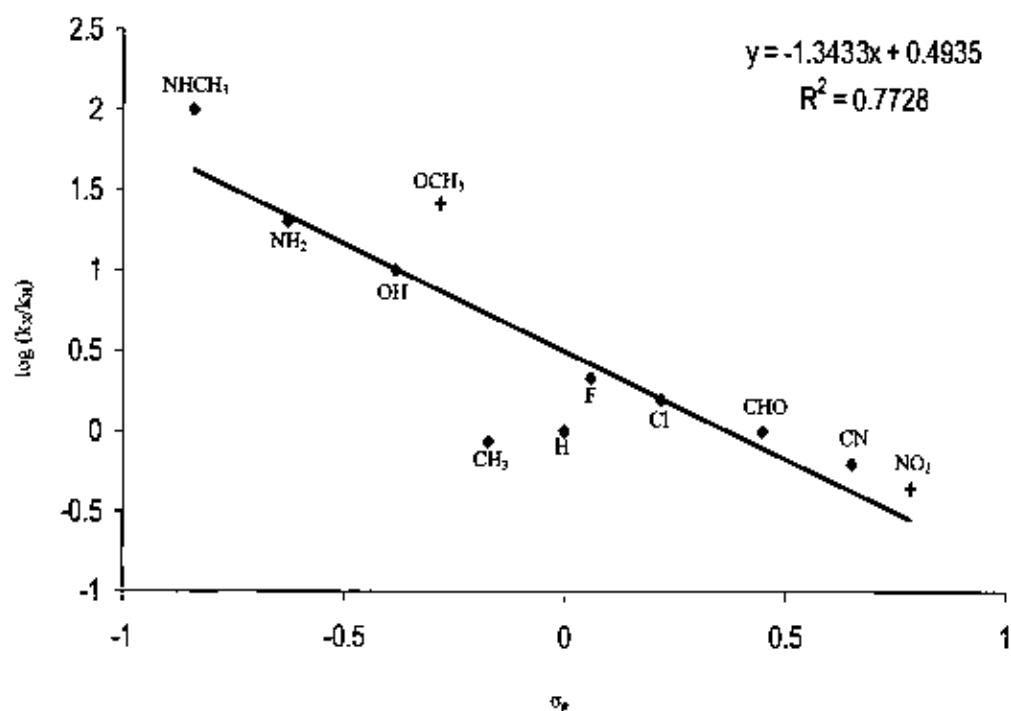
Fig.1. Regression plot between $\log(k_X/k_H)$ and Hammett substituent constant at the para position (σ_p) for the Claisen rearrangement.
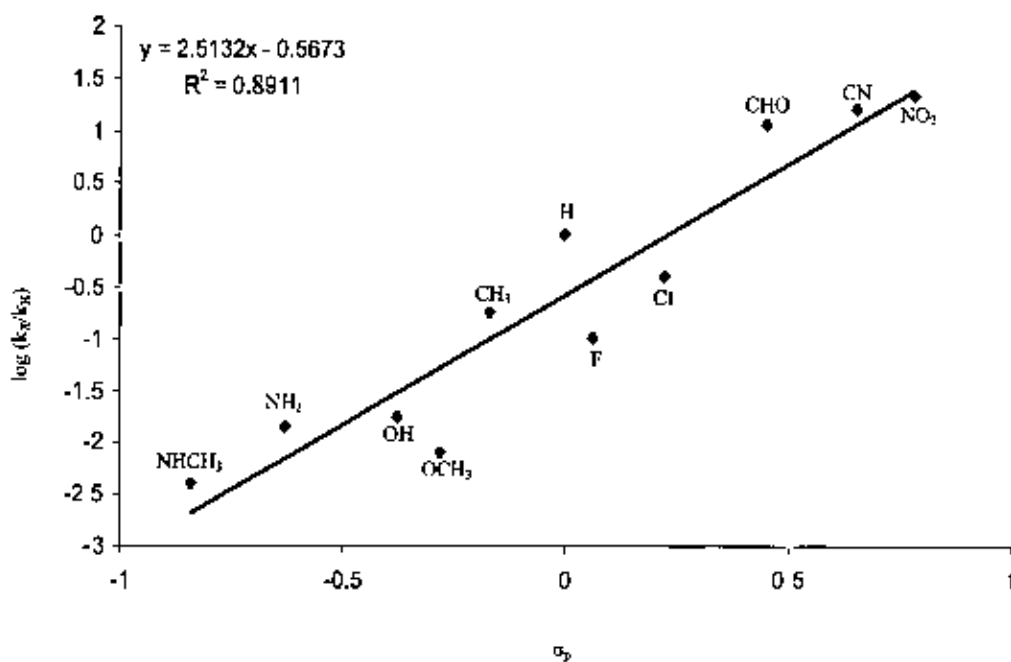

Fig.2. Regression plot between $\log(k_X/k_H)$ and Hammett substituent constant at the para position (σ_p) for the proton shift reaction.

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