Density Functional Theory Studies on the Electrophilic *versus* Electron Transfer Mechanisms of Aryl Vinyl Ethers

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The *ab initio* SCF MO and density functional theory (DFT) studies are carried out on the electrophilic (1a) and electron transfer (1b) addition reactions to the vinyl double bond of aryl vinyl sulfides and ethers. In the electrophilic addition processes, a double bond shift from $C^3 = C^4$ to $X = C^3$ occurs with occupation number (1.97) close to the normal two. Due to this shift direct conjugation between the cationic center, X = S or O, and the para electron-donor substituent becomes impossible so that the reaction energies (or log K) are correlated with σ rather than σ^+. By contrast, radical cation formation leads to delocalization of the SOMO, a lone-pair π orbital on X, with four major resonance structures in which cationic charge as well as spin density is delocalized over C^4, X and C^7 atoms. As a result, partial π bonds are formed over C^1-X and C^3-C^4 with occupation numbers (0.82) lower than one. In two of the cannonical structures, $\mathbf{III}(\dot{X})$ and $\mathbf{III}(\overset{+}{X})$, direct conjugation between the cationic center, X, and the para substituent is achieved so that a better correlation with σ^+ rather than σ is obtained. The SCF MO energies at the HF/3-21G* and HF/6-31G* levels lead to very much inferior Hammett correlations in the σ/σ^+ diagnostic criterion. In contrast, the ρ values evaluated with the DFT energies can give reliable diagnostic distinction between the two addition mechanisms.

Introduction

Aryl vinyl sulfides (**IS**) and ethers (**IO**) are known to react with radical cations by electrophilic additions (EA) to the alkene π bond, not by an electron transfer (ET) mechanism.[1] Diagnosis of the distinction between the electrophilic and electron transfer mechanisms of addition reactions to the vinyl double bond of **I** has been suggested by studying substituent effects and correlating with Hammett σ (EA) and σ^+ (ET) constants, respectively.[1a] This has been ascribed to the important contributions of canonical structure **II** for the electrophilic addition (with an electrophile E[+]) and **III** for the electron transfer mechanism.[1a]

In view of our recent success in correlating substituent effects with the density functional theory (DFT) energies in

the Hammett equation,[2] we carried out DFT calculations to test the σ(EA)/σ^+(ET) dichotomy using typical electrophilic addition reaction, (1a), and electron transfer reaction, (1b).

Calculations

Ab initio molecular orbital calculations were carried out for the electrophilic addition (1a) and electron transfer (1b) processes of aryl vinyl sulfides (**IS**) and ethers (**IO**) with seven substituents, Y, including Y = H using the Gaussian 94 programs.[3] Geometries were optimized without any constraints at the HF/3-21G*, HF/6-31G*[4] and B3LYP/6-31G*[5] levels. In the radical cation formation, the calculations were performed with unrestricted versions[6] of the HF anf B3LYP methods, *i.e.*, UHF and UB3LYP versions. Frequency calculations to confirm stationary states including the transition state (TS) were performed at the former two levels. The Hammett ρ and ρ^+ values were determined using eq. (2) with the reaction energies, ΔE°, estimated at the three respective levels of theory used in the geometry optimization, *e.g*., UB3LYP/6-31G*//UB3LYP/6-31G*[7] for eq. (1b). Numberings of atoms and bonds are shown in Scheme 1.

$$-\frac{\Delta E^\circ}{2.3RT} = \rho\sigma \ (\text{or} \ \ \rho^+\sigma^+) \tag{2}$$

Results and Discussion

The optimized bond lengths at the B3LYP/6-31G* level are collected in Table 1. In the electrophilic addition pro-

$$X \overset{\mathbf{d2}}{=} C^3 H \overset{\mathbf{d3}}{=} C^4 H_2$$
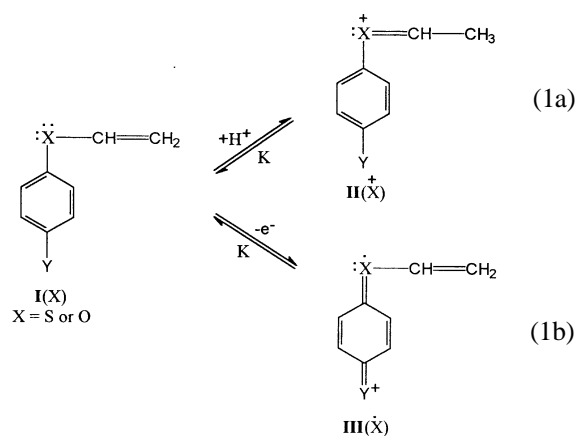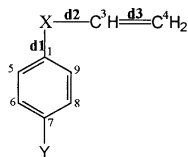
Scheme 1

cesses, (1a), there are two major bond lengths changes: d_2 is contracted whereas d_3 is stretched. There are also minor changes in d_1 for both X = O and S. This corresponds to a change of optimal natural Lewis structure [8] from **I** to **II**. The natural bond orbital (NBO) analysis[8] of **II** shows that π_{X3} orbitals are occupied by nearly two π electrons, 1.972 (ε_{X3} = -0.6538 a.u.) and 1.964 electrons (ε_{X3} = -0.5405 a.u.) for X = O and S, respectively. Thus for the electrophilic addition process, (1a), the cationic center, heteroatom X, forms a single bond with the benzene ring so that direct π-conjugation of the cationic charge with the para substituent Y is not possible.

In contrast, however, the two single bonds, d_1 and d_2, in **I**(X) are contracted while the double bond, d_3, is stretched in the electron transfer process, (1b). The bond length changes are much smaller than those for the electrophilic addition. The overall bond length changes, $\Delta d_1 < 0$, $\Delta d_2 < 0$ and $\Delta d_3 > 0$, indicate that the singly occupied MO (SOMO) of the radical cation system is delocalized over the entire molecule. The NBO analysis[8] showed that the levels of the lone pair π-orbitals on X (n_X) are -0.3139 a.u. (X = O) and -0.2338 a.u. (X = S) which are higher than π_{34} levels by 1.77 eV and 1.99 eV, respectively. Thus the lone pair orbital (n_X) of the heteroatom, X, provides a major component of the SOMO of the radical cation. The NBO analyses have led to optimal natural Lewis structures[8] of the type represented by **III**, in which the cationic center, X, can be directly conjugated with the para substituent Y. The occupancies of π_{1X}, π_{34}, and $p_Z(C^7)$ calculated are 0.902e, 0.783e and 0.293e respectively for X = O and 0.822e, 0.825e and 0.336e respectively for X

= S. These occupancies reflect well the partial nature of the π bonds in the radical cation systems.

The NBO group charges and spin densities at the B3LYP/6-31G* level are summarized in Tables 2 and 3. In both electrophilic addition and electron transfer processes, structures **II** and **III**, the positive charges are predominantly on X, C^4 and C^7 atoms, with very weak positive charge on C^3.

In the electron transfer process, (1b), the spin densities are also large on X, C^4 and C^7 atoms. These trends are in accord with the four canonical structures (with Y = H) for the ET process, **III**($\overset{.}{X}$), **III**($\overset{+}{X}$), **IV**($\overset{.}{X}$) and **IV**($\overset{+}{X}$); radical centers on these four resonance structures are C^4, X and C^7, which are also the cationic charge centers. We note that a direct conjugation is possible between a para electron-donor and the positively charged reaction site, X, in structure **III**($\overset{.}{X}$). The SOMO as well as the cationic charge on the X atom seems to be delocalized over the entire molecule, *i.e.*, toward C^4 and C^7. This is in contrast to the large cationic charge on the side chain in the electrophilic addition products.

The energetics at the B3LYP/6-31G* level is summarized
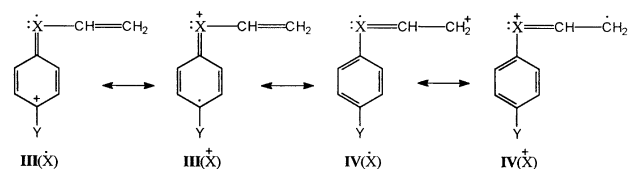
in Table 4. The reaction energies, ΔE°, are used to calculate Hammett ρ values using eq. (2). Similar calculations were carried out with the energies at the HF/3-21G* and HF/6-31G* levels of theory. The ρ values calculated with σ and σ^+ constants[9] are collected in Table 5. Examination of this Table reveals that the linear correlations with the HF SCF MO energies are in general much inferior to those with the DFT (B3LYP/6-31G*) energies. We note that the electrophilic addition processes (1a) correlate better with σ than σ^+, while the electron transfer processes, (1b), correlate better with σ^+

Table 1. Optimized lengths (d in Å) at the B3LYP/6-31G* level for the electrophilic (a) and electron transfer (b) processes

	Y	Reactant			$\Delta d(a)$			$\Delta d(b)$		
		d_1	d_2	d_3	Δd_1	Δd_2	Δd_3	Δd_1	Δd_2	Δd_3
X = O	NH$_2$	1.3839	1.3698	1.3315	0.0126	-0.0975	0.1390	-0.0499	0.0093	0.0017
	OCH$_3$	1.3616	1.3708	1.3311	0.0252	-0.1025	0.1376	-0.0474	0.0041	0.0050
	CH$_3$	1.3793	1.3719	1.3307	0.0447	-0.1072	0.1355	-0.0408	-0.0078	0.0119
	H	1.3783	1.3726	1.3305	0.0538	-0.1090	0.1342	-0.0346	-0.0162	0.0173
	Cl	1.3749	1.3748	1.3299	0.0475	-0.1089	0.1350	-0.0372	-0.0098	0.0129
	CN	1.3678	1.3780	1.3290	0.0617	-0.1125	0.1338	-0.0264	-0.0204	0.0189
	NO$_2$	1.3654	1.3792	1.3287	0.0683	-0.1144	0.1332	-0.0161	-0.0319	0.0261
X = S	NH$_2$	1.7917	1.7774	1.3354	-0.0450	-0.1320	0.1494	-0.0582	-0.0090	0.0023
	OCH$_3$	1.7921	1.7762	1.3354	-0.0350	-0.1313	0.1469	-0.0594	-0.0247	0.0084
	CH$_3$	1.7911	1.7749	1.3353	-0.0202	-0.1297	0.1440	-0.0568	-0.0327	0.0131
	H	1.7914	1.7749	1.3352	0.0038	-0.1292	0.1426	-0.0530	-0.0382	0.0164
	Cl	1.7890	1.7756	1.3350	-0.0158	-0.1292	0.1433	-0.0529	-0.0339	0.0140
	CN	1.7836	1.7760	1.3346	-0.0012	-0.1286	0.1417	-0.0445	-0.0397	0.0177
	NO$_2$	1.7809	1.7762	1.3345	0.0064	-0.1283	0.1407	-0.0375	-0.0460	0.0213

Table 2. Calculated group charges (q) in electron unit by NPA at the B3LYP/6-31G* for the electrophilic (a) and electron transfer (b) processes

	Y	Reactant				$\Delta q(a)$				$\Delta q(b)$			
		q_X	q_3	q_4	q_7	Δq_X	Δq_3	Δq_4	Δq_7	Δq_X	Δq_3	Δq_4	Δq_7
	NH_2	-0.512	0.312	-0.066	0.153	0.144	0.329	0.164	0.068	0.096	-0.001	0.191	0.072
	OCH_3	-0.510	0.310	-0.059	0.303	0.144	0.365	0.167	0.078	0.109	0.010	0.209	0.113
	CH_3	-0.509	0.311	-0.055	-0.053	0.145	0.401	0.176	0.079	0.171	0.031	0.240	0.158
X = O	H	-0.509	0.310	-0.051	-0.255	0.145	0.421	0.178	0.070	0.139	0.049	0.262	0.153
	Cl	-0.507	0.306	-0.041	-0.063	0.141	0.412	0.168	0.035	0.125	0.037	0.234	0.069
	CN	-0.501	0.304	-0.026	-0.194	0.135	0.436	0.162	0.075	0.128	0.056	0.246	0.133
	NO_2	-0.498	0.303	-0.019	0.034	0.132	0.447	0.159	0.055	0.138	0.081	0.267	0.123
	NH_2	0.391	-0.161	-0.006	0.173	0.449	0.128	0.124	0.058	0.295	-0.032	0.176	0.061
	OCH_3	0.309	-0.166	0.002	0.321	0.443	0.165	0.126	0.070	0.345	-0.015	0.190	0.094
	CH_3	0.319	-0.172	0.010	-0.036	0.433	0.205	0.127	0.074	0.381	-0.005	0.212	0.125
X = S	H	0.322	-0.170	0.015	-0.239	0.428	0.219	0.126	0.067	0.401	-0.003	0.227	0.118
	Cl	0.328	-0.173	0.024	-0.050	0.424	0.215	0.118	0.032	0.373	-0.003	0.206	0.053
	CN	0.346	-0.177	0.042	-0.181	0.404	0.239	0.107	0.072	0.379	0.004	0.210	0.109
	NO_2	0.354	-0.178	0.047	0.045	0.395	0.251	0.105	0.055	0.395	0.010	0.224	0.096

Table 3. Calculated Mulliken Spin Densities at the B3LYP/6-31G* level for the electron transfer process, eq (1b)

	Y	C^4	C^3	X	C^7
	NH_2	0.166	-0.050	0.161	0.130
	OCH_3	0.203	-0.051	0.184	0.189
	CH_3	0.275	-0.051	0.216	0.313
X = O	H	0.327	-0.046	0.235	0.313
	Cl	0.274	-0.044	0.210	0.255
	CN	0.316	-0.034	0.219	0.276
	NO_2	0.382	-0.027	0.243	0.265
	NH_2	0.126	-0.057	0.299	0.108
	OCH_3	0.227	-0.081	0.353	0.151
	CH_3	0.283	-0.088	0.410	0.238
X = S	H	0.316	-0.090	0.440	0.233
	Cl	0.284	-0.083	0.405	0.196
	CN	0.313	-0.080	0.427	0.212
	NO_2	0.349	-0.081	0.460	0.199

Table 4. Calculated electronic energies (E in hartree) and reaction energies (ΔE^o in kcal mol^{-1}) at the B3LYP/6-31G* level for electrophilic (a) and electron transfer (b) processes

	Y	E			$\Delta E^o(a)$	$\Delta E^o(b)$
		I(X)	II(X)	III(X)		
	NH_2	-440.20657	-440.57528	-439.96191	-231.37	153.53
	OCH_3	-499.37628	-499.73690	-499.11661	-226.29	162.95
	CH_3	-424.17295	-424.52881	-423.89977	-223.31	171.42
X = O	H	-384.85531	-385.20707	-384.57332	-220.73	176.95
	Cl	-844.45055	-844.79665	-844.16753	-217.18	177.60
	CN	-477.09934	-477.43454	-476.80097	-210.34	187.23
	NO_2	-589.35806	-589.69006	-589.05185	-208.33	192.15
	NH_2	-763.18201	-763.55213	-762.93893	-232.25	152.54
	OCH_3	-822.35094	-822.71390	-822.09418	-227.76	161.12
	CH_3	-747.14658	-747.50424	-746.87941	-224.44	167.65
X = S	H	-707.82846	-708.18207	-707.55434	-221.89	172.01
	Cl	-1167.42401	-1167.77235	-1167.14730	-218.59	173.64
	CN	-800.07188	-800.40985	-799.78184	-212.08	182.00
	NO_2	-912.33046	-912.66536	-912.03458	-210.15	185.67

Table 5. Calculated Hammett reaction constants, ρ

	Basis set	Electrophilic Addition		Electron Transfer	
		ρ	ρ^+	ρ	ρ^+
	HF/3-21G*	-11.21±0.60 ($r = 0.99_3$)	-7.42±1.01 ($r = 0.95_6$)	-17.93±1.96 ($r = 0.97_1$)	-12.36±1.25 ($r = 0.97_5$)
X = O	HF/6-31G*	-10.05±0.84 ($r = 0.98_3$)	-6.58±1.09 ($r = 0.93_8$)	-17.83±1.29 ($r = 0.98_7$)	-12.23±0.92 ($r = 0.98_6$)
	B3LYP/3-31G*	-11.87±0.29 ($r = 0.99_9$)	-8.04±0.63 ($r = 0.98_5$)	-18.64±1.79 ($r = 0.97_8$)	-13.06±0.39 ($r = 0.99_8$)
	HF/3-21G*	-10.04±0.57 ($r = 0.99_2$)	-6.65±0.91 ($r = 0.95_6$)	-12.18±1.22 ($r = 0.97_6$)	-8.23±1.08 ($r = 0.96_0$)
X = S	HF/6-31G*	-9.45±0.71 ($r = 0.98_6$)	-6.22±0.97 ($r = 0.94_5$)	-12.25±0.92 ($r = 0.98_6$)	-8.27±0.92 ($r = 0.97_0$)
	B3LYP/3-31G*	-11.44±0.38 ($r = 0.99_7$)	-7.77±0.57 ($r = 0.98_7$)	-16.14±1.30 ($r = 0.98_4$)	-11.24±0.28 ($r = 0.99_9$)

rather than with σ. The distinction between the two mechanisms based on the σ/σ^+ correlations[1a] becomes clear only with the DFT results. Thus in the electrophilic addition processes a direct resonance interaction between the cationic center, $\overset{+}{X}$, and the para electron-donor, Y, is not possible, whereas it is possible in the electron transfer processes.

The magnitude of the two ρ values (ρ for EA and ρ^+ for ET) are, however, quite similar, $\rho = -11.4$ and $\rho^+ = -11.2$ for X = S, and $\rho = -11.9$ and $\rho^+ = -13.1$ for X = O at B3LYP level. Since these ρ values are for the gas-phase reactions, the magnitudes are much greater than those in solution. For example, the ρ values reported are as follow: For the acid-catalyzed hydrolysis in 50% dioxane-water at 25 ºC $\rho = -2.00$ (X = O), -1.84 (X = S) and -1.55 (X = Se),[10] and in 80% dioxane-water $\rho = -2.14$ (X = O) at 25 ºC.[11] For the trifluoroacetylation in CDCl$_3$ at 35 ºC $\rho = -2.4$.[12] The ρ values for the electrophilic additions of the 2,5-dimethylhexa-2,4-diene radical cation and the tetracyanoethene to aryl vinyl sulfides are $\rho = -2.56$ and -3.62, respectively.[1a] These ρ values are for the activation processes in solution so that those for the corresponding equilibrium processes of proton addition in solution should be larger, *approximately* by a factor of two assuming *ca.* 50% progress of the reaction in the transition state. Thus it appears that $\rho_{(gas)} \simeq (2\sim3) \times \rho_{(soln)}$, which is quite reasonable since a much lower substituent effect is expected in solution than in the gas phase on the grounds of the appreciable stabilization of the cationic charges through solvation, *i.e.*, by a solvent attenuation of the substituent effect. For the protonation equilibria of substituted acetophenones, the gas phase ρ value was greater by a factor of 5.9 than that in water at 25 ºC.[13] In this case, the factor is greater, since protonation occurs at the much more basic oxygen atom in contrast to protonation on a vinylic carbon in **I** and **II**.

In summary, the electrophilic additions to aryl vinyl sulfides and ethers, (1a), proceed by a TS or product structure with the positive charge localized on the X = S or O atom, **II**, and a shift of double bond from C^3-C^4 to C^1-X so that direct conjugation between para substituent and the cationic center X becomes impossible.

In contrast, radical cation formation in a series of **I**(S) and **I**(O) leads to delocalization of the SOMO, which is a lone-pair π orbital, over entire molecule with four major resonance structures of **III**($\overset{.}{X}$), **III**($\overset{+}{X}$), **IV**($\overset{.}{X}$) and **IV**($\overset{+}{X}$). As a result, cationic charge as well as spin density is largely delocalized over C^4, X and C^7 atoms and the reaction energies are better correlated with σ^+ rather than σ. Diagnosis of the distinction between the electrophilic (correlation with σ) and electron transfer mechanisms (correlation with σ^+) is diffi-

cult with the uncorrelated SCF MO energies; by contrast the DFT calculations provide an excellent means of estimating the Hammett ρ values and diagnostic distinction between the two addition mechanisms.

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