BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2316—2320 (1973)

Transmission of Substituent Effects through the Oxygen and Sulfur Atoms. IV. CNDO/2 Charge Distributions in Vinyl and Divinyl Ethers and Sulfides

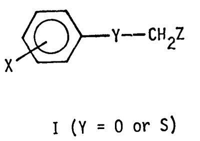
Okitsugu Kajimoto, Masaru Kobayashi, and Takayuki Fueno
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received April 13, 1973)

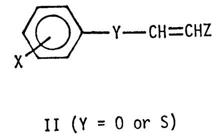
Charge distributions in vinyl methyl and divinyl ethers and their sulfur homologs bearing a polar substituent at the *trans*-β position were calculated by the CNDO/2 method. It was found that the effect of substituents on charge distribution is transmitted primarily through the successive π-polarization of the ethylenic units involved. In the divinyl compounds, the sulfur atom on the spd basis is calculated to transmit the substituent effects more effectively than the oxygen atom. The greater transmission efficiency of the sulfur atom is interpreted in terms of the pπ-dπ-pπ conjugation.

The reaction constant ρ of the Hammett equation is a useful experimental probe into the mode and efficiency of the transmission of the electronic effects of substituents in aromatic side-chain reactions.[1,2] A systematic examination of the ρ-values often permits quantitative comparison of the transmission efficiencies of the atoms or groups which intervene between reaction center and substituents.[3]

In the preceding papers of this series,[4-6] we compared the roles of the oxygen (Y=O) and sulfur (Y=S) atoms in transmitting the effects of ring-substituents (X) to the properties of the side-chain groups (CH_2Z and CH=CHZ) in two types of compounds I and II:



I (Y = O or S)



II (Y = O or S)

The properties investigated were the ^1H chemical shifts of the terminal hydrogen (Z=H),[4] the ^{13}C shifts of the aliphatic carbons (CH_2Z and CH=CHZ with Z=H),[5] and the ionization equilibrium constants of the carboxylic acids (Z=COOH).[6] It was found that, while in compounds I the sulfur atom is apparently a less efficient transmitter of the substituent effects than the oxygen atom, it becomes a more efficient transmitter in compounds II in which it is interposed between two unsaturated groups. The enhancement of the transmission efficiency of the sulfur atom was interpreted in terms of the pπ–dπ–pπ interaction, i.e., the "through-conjugative" contribution[7]

---

[1] L. P. Hammett, "Physical Organic Chemistry," 2nd Ed. McGraw-Hill Book Company, New York, N. Y. (1970).

[2] H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

[3] S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

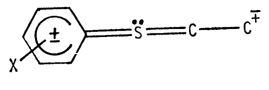
[4] T. Fueno, O. Kajimoto, K. Izawa, and M. Masago, This Bulletin, **46**, 1418 (1973).

[5] O. Kajimoto, M. Kobayashi, and T. Fueno, *ibid.*, **46**, 1422 (1973).

[6] O. Kajimoto, M. Kobayashi, and T. Fueno, *ibid.*, **46**, 1425 (1973).

[7] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y. (1962).

of the sulfur 3d-orbitals to the π-conjugation as can be represented by III.



III

The purpose of the present paper is to rationalize the qualitative view stated above. Thus, we have undertaken to calculate the CNDO/2 charge distributions in various β-substituted derivatives of methyl vinyl (IV) and divinyl (V) ethers and their corresponding sulfur homologs, which may be regarded as the model compounds of I and II, respectively.

$$XCH{=}CH{-}Y{-}CH_3 \qquad XCH{=}CH{-}Y{-}CH{=}CH_2$$

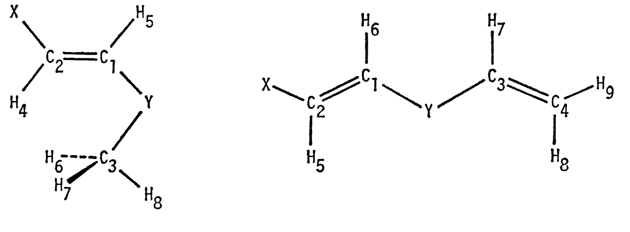
IV (Y = O or S) V (Y = O or S)

The results of calculation based on the spd basis set for the sulfur atom were found to be compatible with the substituent effects observed.

Method

Pople's CNDO/2 method[8] was used without modification. The sulfur atom was treated on both the sp and spd bases; the integral parameters were those determined by Santry and Segal.[9]

The molecular geometries and atomic numberings of IV and V are shown in Fig. 1. IV was assumed to be in the *s-cis* conformation[10] with the methyl C–H bonds directed as shown in Fig. 1, while V was assumed to have the *s-trans,s-trans* conformation which should apparently be the most stable planar form. In both IV and V, the β-substituent X was placed at a position *trans* to the atom Y. The substituents chosen for this study were the CH_3O, CH_3, H, F, and Cl atoms or groups. For the Cl atom, the 3d-orbitals were included throughout. All the necessary bond lengths were taken from the literature.[8]



IV V

Fig. 1. Molecular geometries and atomic numberings of IV and V. The carbon atoms were assumed to have either sp^2 or sp^3 valence angles, and the CYC bond angles were assumed to be 110 and 105° for Y=O and Y=S, respectively.

Calculations were carried out on a NEAC 2200 computer at the Osaka University Computation Center. The outputs were required to be self-consistent to within 10^{-4} for all the atomic-orbital densities.

Results

The charge distributions calculated for the various derivatives of IV and V are summarized in Tables 1 and 2, respectively. The entries there are the net charge densities, both total and π, defined by

$$Q_r = n_r - q_r \qquad (1)$$

where q_r is the pertinent electron density on atom r and where n_r is the number of its relevant valence electrons. The spd basis set was used for the sulfur atom, but, for the sake of comparison, calculations based on the sp basis were also carried out for divinyl sulfides. The results of the latter calculations are given in parentheses (Table 2).

Discussion

A. Charge distribution in Unsubstituted Compounds. Previous studies[3–5] on the ^1H and ^{13}C chemical shifts in ethers and sulfides have shown that an oxygen atom apparently behaves as a π-donor-σ-acceptor while a sulfur atom tends to act as a π,σ-acceptor. The view can readily be tested by analyzing the π and σ-charge densities on the oxygen and sulfur atoms. In Fig. 2, the amount of electronic charge transferred to or from these atoms in divinyl ether and sulfide are illustrated.[11] It can be seen that the oxygen atom strongly with-

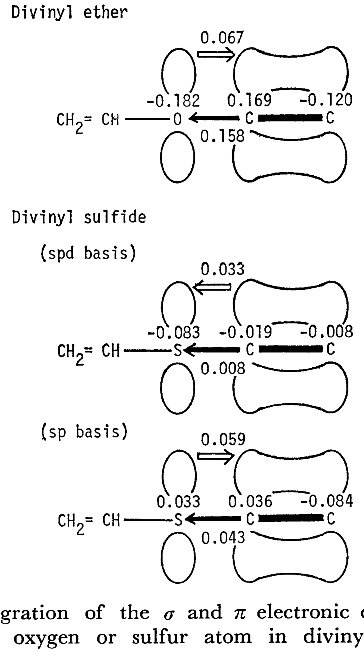


Fig. 2. Migration of the σ and π electronic charges from or to the oxygen or sulfur atom in divinyl ether and sulfide.

---

[8] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Book Company, Inc., New York (1970).

[9] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

[10] N. L. Owen and N. Sheppard, *Trans. Faraday Soc.*, **60**, 634 (1964).

[11] The amount of electronic charge transferred *from* the $p\pi$-orbital of the oxygen or sulfur atom *to* one of the ethylenic π-bonds can be obtained by dividing the π charge density Q_Y^π (Table 2) by 2. Likewise, one half the σ charge density on Y ($Q_Y^\sigma = Q_Y - Q_Y^\pi$) may be defined as the amount of the σ charge migration *from* Y *to* one of the olefinic groups.

TABLE 1. TOTAL AND π CHARGE DENSITIES ($\times 10^4$) IN SUBSTITUTED VINYL METHYL ETHERS AND SULFIDES (IV)

Position	Y=O					Y=S				
	CH_3O	CH_3	H	F	Cl	CH_3O	CH_3	H	F	Cl
	Total charge density									
C_1	721	1398	1637	940	1816	−1124	−416	−202	−982	−100
C_2	721	−10	−1305	1129	−512	1881	411	−67	2304	627
C_3	1388	1422	1429	1367	1394	−657	−629	−626	−676	−645
H_4	135	192	263	160	448	111	145	222	125	395
H_5	135	17	6	249	189	511	370	399	655	576
$H_{6,7}$	−116	−102	−81	−78	−38	270	283	313	316	354
H_8	−72	−86	−80	−9	5	370	365	382	429	444
Y	−1941	−2001	−1973	−1838	−1867	−926	−982	−853	−656	−645
	π-Charge density									
$C_1\pi$	−629	88	457	−210	781	−936	−229	172	−488	413
$C_2\pi$	−629	−869	−1189	−875	−1205	690	178	152	431	30
$Y\pi$	874	962	970	912	1061	−976	−805	−731	−882	−651

TABLE 2. TOTAL AND π CHARGE DENSITIES ($\times 10^4$) IN SUBSTITUTED DIVINYL ETHERS AND SULFIDES (V)

Position	Y=O					Y=S[a]				
	CH_3O	CH_3	H	F	Cl	CH_3O	CH_3	H	F	Cl
	Total charge density									
C_1	754	1439	1689	972	1860	−1111 (−553)	−402 (135)	−189 (359)	−971 (−370)	−82 (506)
C_2	837	−649	−1204	1245	−425	1880 (1143)	410 (−334)	−77 (−838)	2302 (1547)	−616 (−68)
C_3	1713	1698	1689	1699	1669	−166 (383)	−176 (370)	−189 (359)	−169 (368)	−189 (339)
C_4	−1238	−1226	−1204	−1180	−1134	−120 (−868)	−107 (−853)	−77 (−838)	−59 (−820)	−13 (−773)
H_5	161	231	313	192	490	85 (17)	130 (68)	213 (139)	103 (37)	388 (321)
H_6	−9	−130	−138	107	32	444 (199)	295 (66)	322 (68)	581 (317)	491 (247)
H_7	−156	−149	−138	−109	−97	294 (53)	303 (59)	322 (68)	350 (93)	363 (108)
H_8	301	303	313	325	343	200 (131)	201 (132)	213 (139)	226 (150)	243 (166)
H_9	238	239	250	276	295	129 (100)	130 (101)	148 (111)	175 (135)	194 (155)
Y	−1817	−1856	−1818	−1736	−1741	−945 (276)	−969 (254)	−834 (325)	−720 (434)	−676 (503)
	π-Charge density									
$C_1\pi$	−720	−12	370	−287	693	−928 (−860)	−220 (−127)	176 (248)	−481 (−420)	425 (560)
$C_2\pi$	−491	−719	−1040	−747	−1061	690 (−308)	451 (−545)	156 (−842)	428 (−566)	33 (−904)
$C_3\pi$	406	394	370	337	284	217 (273)	207 (265)	176 (248)	152 (218)	109 (170)
$C_4\pi$	−1089	−1073	−1040	−994	−925	85 (−887)	109 (−866)	156 (−842)	187 (−807)	262 (−732)
$Y\pi$	1253	1336	1339	1274	1410	−892 (1111)	−729 (1192)	−664 (1188)	−820 (1138)	−604 (1284)

[a] The data given in parentheses are those obtained by using the sp basis set for the sulfur atom.

draws σ-electron from the neighboring carbon atoms but donates π-electron to the ethylenic π-bond. On the other hand, the sulfur atom (spd) accepts a small fraction of electron from both the σ and π orbitals of ethylene. The π-electron-accepting property of the sulfur atom is ascribable to the participation of its 3d-orbitals in π-conjugation; the sulfur atom on the sp basis is predicted to be π-electron-donating, as can be seen in Fig. 2.

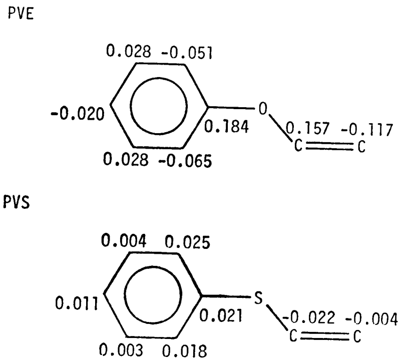


Fig. 3. The charge density distributions in phenyl vinyl ether (PVE) and sulfide (PVS).

Figure 3 shows the calculated total charge densities on the skeletal carbon atoms in phenyl vinyl ether (PVE) and sulfide (PVS). The charges in the vinyl moiety of these compounds are much the same as those in divinyl compounds. This endorses the validity of using the divinyl compounds as the model for PVE and PVS. In both types of compounds, the α-carbon atom of the sulfides are calculated to have a greater electron density than the β-carbon, in contrast to the greater electron density on the β-carbon in the unsaturated ethers.

The charge distributions shown in Fig. 3 are also to be compared with the ^{13}C chemical shift data presented previously.[5)] In Fig. 4 the total electron densities q_r of the various carbon atoms in PVE and PVS are plotted against the ^{13}C chemical shifts. For the purpose of comparison, the data of benzene[12)] has also been plotted. The points for the PVS derivatives gather in the vicinity of the plot for benzene, while those for PVE's are spread in a relatively wide range of q_r. The latter points are roughly fitted by a straight line with the slope of 175 ppm/electron, which is in fair agreement with the value 155 ppm/electron reported by Tokuhiro and Fraenkel[13)] for azines.

B. Substituent Effects in Divinyl Ethers. The electronic effects of *trans-β* substituents on the charge distribution in divinyl ethers are expected to resemble those of *para* substituents in phenyl vinyl ethers. In Fig. 5, the π, σ, and total electron densities (q^π, q^σ, and q, respectively) on the α- and β-carbons of the various divinyl ether derivatives are plotted against the Hammett constants for *para* substituents, σ_p. Although the substituents studied are limited in number, it appears that all the calculated densities are linearly correlated with σ_p.

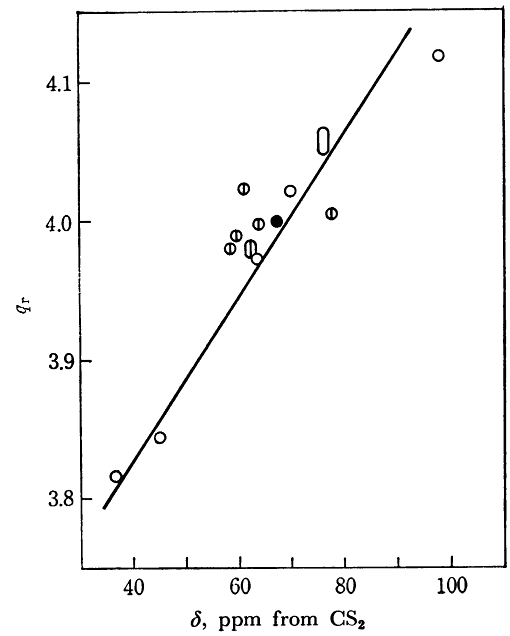


Fig. 4. Parallelism between the ^{13}C chemical shifts and the calculated total electron densities on carbon atoms of phenyl vinyl ether (PVE) and sulfide (PVS). ○, PVE; ⦶, PVS; ●, Benzene.

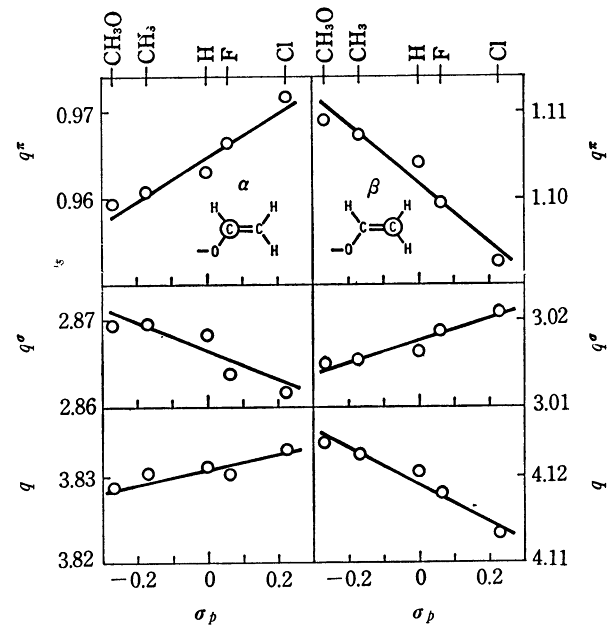


Fig. 5. The π, σ and total electron densities on the α- and β-carbons of substituted divinyl ethers.

The linear relationship shown in Fig. 5 are worthy of note in two important respects. First, the effects of substituents on the total electron density at the α- and β-carbons (q_α and q_β) are opposite in direction to each other; the electron-donating substituents tend to diminish q_α whereas they clearly enhance q_β. The results are in line with our previous observation that the ^{13}C chemical shifts, δ, of the α-carbon of PVE shows a Hammett-type dependence on ring substituents with a positive slope of $\rho_\alpha=3.10\ \delta/\sigma$, in contrast to a "nor-

---

12) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **90**, 6537 (1968).

13) T. Tokuhiro and G. Fraenkel, *ibid.*, **91**, 5005 (1969).

mal" negative slope of $\rho_\beta = -4.84\ \delta/\sigma$ for the β-carbon.[5] A similar phenomenon, which was referred to as the "inverse" substituent effects, was observed for the γ- and δ-carbon atoms in *trans*-1-substituted-1,3-butadienes and rationalized in terms of the CNDO/2 total charge density.[14]

The second point which should be noted is that the substituent effects on the total electron density, q, is governed primarily by those on the π-electron density, q^π. The plots of the σ-electron density, q^σ, give slopes opposite in sign to those of q^π, and their dependence on substituents is relatively small. This would mean that, at least in the side-chain sp^2 carbons, any increase in q^π effected by substituents should be accompanied by a compensating decrease in q^σ which should, however, be overshadowed by the increase in q^π. In effect, therefore, the π-framework is considered to constitute a main route for the transmission of substituent effects in the case of unsaturated compounds. The electronic effect of substituents should thus be transmitted along the bonds through successive π-polarization of the ethylenic unit.[15] This in turn accounts for the inverse substituent effects as has been discussed in the last paragraph.

C. Transmission Efficiencies of the Oxygen and Sulfur Atoms. We now compare the efficiencies of the oxygen and sulfur atoms in transmitting the substituent effects. For this purpose, we will plot the total electron densities, $q_r(S)$, calculated for given positions (r) of the various derivatives of vinyl or divinyl sulfide against those obtained for the corresponding ethereal derivatives, $q_r(O)$. If such "O–S plots" are linear over the substituents studies, their slopes, *viz.*,

$$R_r = dq_r(S)/dq_r(O) \qquad (2)$$

may be regarded as a theoretical measure of the transmission efficiency of the sulfur atom relative to the oxygen atom.

Figure 6 shows the O–S plots for the terminal hydrogens H_8 and H_9 in vinyl methyl (IV) and divinyl compounds (V), respectively. The slope for the former hydrogen is $R_8 = 0.825$, indicating that the sulfur atom is a less efficient transmitter of substituent effects onto this particular hydrogen atom. By contrast, the *trans*-β hydrogen (H_9 of V in the spd approximation) has a slope of $R_9 = 1.139$, indicative of a greater transmission efficiency of the sulfur atom. It should be noted that the sulfur atom is calculated to be a less efficient transmitter ($R_9 = 0.956$) when its 3d-orbitals are left out of consideration (dashed line).

The O–S plots for the β-carbon atom in divinyl compounds are shown in Fig. 7. The slope is found to be $R_\beta = 1.020$ when the spd basis set was used for the sulfur atom, while it is $R_\beta = 0.885$ in the case of the sp approximation. Thus, the sulfur atom cannot be a more efficient transmitter of substituent effects than the oxygen atom, unless the 3d-orbitals of sulfur partake in the construction of the molecular orbitals.

In previous papers,[4–6] we demonstrated experimentally that the sulfur atom can transmit the substituent effects more efficiently than the oxygen atom, when it is interposed between two unsaturated groups. It was then inferred that the 3d-orbitals of the sulfur atom should play an essential and decisive role in this enhancement in the transmission efficiency. The theoretical results given in Figs. 6 and 7 are well in line with these experimental deductions. This reinforces our concept that the through-conjugative participation (III) of the sulfur 3d-orbitals in π-conjugation, *i.e.*, the pπ–dπ–pπ conjugation, is of distinct importance to the transmission of substituent effects in the compounds in which the sulfur atom is interposed between two unsaturated groups.[4,5]

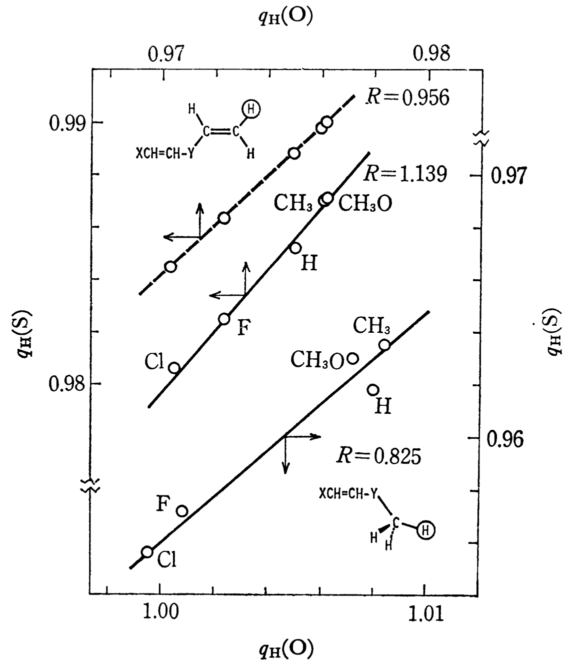


Fig. 6. "O–S plots" of the electron densities for the terminal hydrogens. R denotes the slope of each line. ——, spd basis; ----, sp basis.

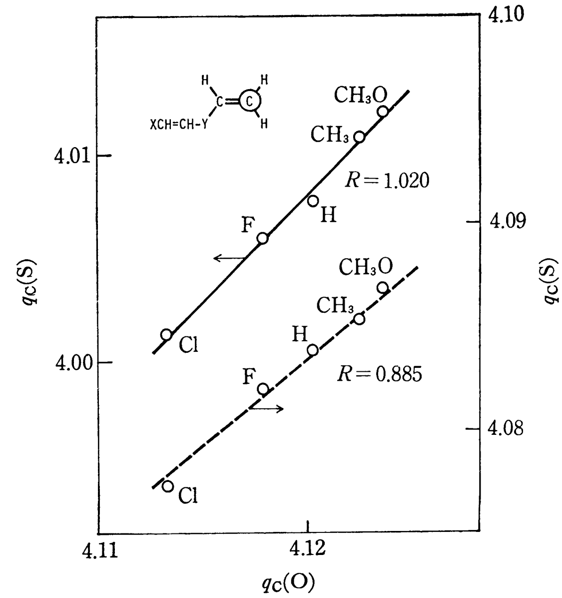


Fig. 7. "O–S plots" of the electron densities for the β-carbon atom. R denotes the slope. ——, spd basis; ----, sp basis.

---

[14] O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, **1972**, 3329.

[15] The successive polarization of π-bondings is a well-known characteristics of conjugated molecules in general. The intervention of an oxygen atom does not affect this mode of transmission of the substituent effects.