Transmission of Substituent Effects through Oxygen and Sulfur Atoms. I. ^{1}H Chemical Shifts of Ring-substituted Phenyl Vinyl Ethers and Sulfides

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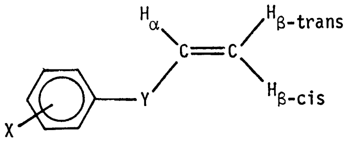
The proton chemical shifts of the vinyl group in ring-substituted phenyl vinyl ethers (PVE) and sulfides (PVS) were measured and related to the Hammett σ constants. It was found that the ρ value for the *β-trans* proton of PVS, $-0.448\ \tau/\sigma$, is greater in magnitude than that of PVE, $-0.378\ \tau/\sigma$, in contrast to the tendency reported for the methyl hydrogens in anisole and thioanisole. The results can best be explained in terms of the concept of the through-conjugative (pπ-dπ-pπ) behavior of the sulfur atom interposed between two unsaturated groups.

The transmission of substituent effects has been a subject of continuous interest to organic chemists ever since Hammett's proposal of the $\rho\sigma$ relationship.[1] One of the recent problems in this field concerns the role of d-orbitals in transmitting the electronic effects of substituents. Marcus *et al.*[2] summarized numerous reports on the Hammett dependence of ^{1}H chemical shifts in compounds of the XC_6H_4T–H type, in which X is the substituent, and C_6H_4T, the transmitting group. Particular attention was paid to oxygen and sulfur when they form part of T. Thus, by comparing the ρ-values for phenol (T=O) and anisole ($T=OCH_2$) with those for the corresponding sulfur analogs, *i.e.*, thiophenol (T=S) and thioanisole ($T=SCH_2$), they found that the efficiency of oxygen in transmitting the substituent effects is generally greater than that of sulfur. They also discussed the transmission efficiencies of these atoms by citing several experimental results other than ^{1}H chemical shifts and commented that the sulfur atom must show greater efficiency when it acts as an electron acceptor in conjugated systems ("conjugative-acceptor case"). At that time, however, no appropriate and decisive example was available.

The present series of investigations was undertaken in order to look into the mode of the transmission of substituent effects through the sulfur atom both experimentally and theoretically, and thereby to elucidate the mechanism of transmission in relation to the nature of sulfur bondings. In this paper, we will compare the substituent effects on the ^{1}H chemical shifts of vinyl hydrogens in ring-substituted phenyl vinyl ethers (I; Y=O) and sulfides (I; Y=S). These compounds are characterized by the intervention of an oxygen or divalent sulfur atom between two unsaturated moieties, thus fulfilling Marcus' condition for the "conjugative-acceptor case." For the sake of comparison, the ^{1}H chemical shifts of ring-substituted allylbenzenes and styrenes were also measured.



(Y = O,S) I

Experimental

Materials. Ring-substituted phenyl vinyl ethers,[3] phenyl vinyl sulfides,[4] and styrenes[5] were synthesized according to the methods given in the literature. Ring-substituted allylbenzenes were prepared from allyl bromide and the corresponding bromobenzenes through Grignard coupling; the boiling points (°C/mmHg) of the products were: *p*-CH_3O 83/9.5, *p*-CH_3 75/23.5, *m*-CH_3 60/10, H 156—157/760, *p*-Cl 82/15.5 and *m*-Cl 83/25.

NMR Measurements. The NMR spectra were recorded on a JNM 4H-100 spectrometer (JEOL) operating at a frequency of 100 MHz. All the compounds were examined at room temperature as 10% (by volume) solutions in CCl_4. The chemical shifts did not vary significantly with concentration, and they were accurate to within ±0.05 Hz. TMS was used as the internal standard.

Assignment of Signals. The NMR signals for the ethylenic *α*, *β-cis*, and *β-trans* protons of phenyl vinyl ethers and sulfides appear as three quartets. They were assigned to the relevant protons on the basis of the well-known differences in the coupling constants, J_{gem}, J_{trans}, and J_{cis}. The chemical shifts were determined as the mean value of each set of quartet peaks. The ABX system analysis was also carried out by computer calculations; this confirmed the results. In the case of allylbenzenes, the singals of the ethylenic protons were split into three sets of twelve peaks. The complicated signals were analyzed by computer calculations for a 5-spin system.

Results

Table 1 summarizes the H–H coupling, J (Fig. 1), for phenyl vinyl sulfide (PVS), phenyl vinyl ether (PVE), allylbenzene (ABz), and styrene (St). The values of J are not sensitive to ring-substitution within the limits of experimental error.

The chemical shifts, τ, observed for the vinyl protons are listed in Table 2. It can be seen that the τ-values

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y. (1940), Chapter 7.

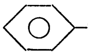
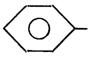
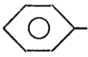
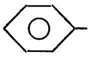
[2] S. H. Marcus, W. F. Reynold, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

[3] S. M. McElvain and B. Fajardo-Pinzon, *J. Amer. Chem. Soc.*, **67**, 650 (1945).

[4] H. Meerwein, *Chem. Ber.*, **90**, 841 (1957).

[5] W. S. Emerson, *Chem. Rev.*, **49**, 347 (1949).

Table 1. Coupling constants for some compounds (in Hz)

	J_{gem}	J_{trans}	J_{cis}	$J_{\alpha\text{-CH}_2}$	J_{allyl}
-O-CH=CH$_2$	−1.5	13.8	6.0		
-S-CH=CH$_2$	0	16.4	9.4		
-CH$_2$-CH=CH$_2$	1.9	17.4	9.6	6.6	−1.6
-CH=CH$_2$	1.1	17.5	10.7		

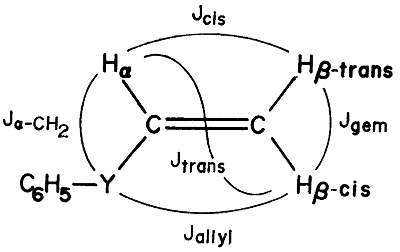


Fig. 1. Couplings between side-chain protons in $C_6H_5YCH{=}CH_2$.

tend to decrease with the increase in the electron-accepting ability of the substituents.

In Fig. 2, the chemical shifts of the *β-trans*, *β-cis*, and α protons of PVE derivatives are plotted against the Hammett σ constans of the substituents. Least-squares fits of the plots to the linear relationships, $\tau_X - \tau_H = \rho\sigma$, resulted in the sensitivity constants, ρ, of −0.378, −0.324, and −0.121 τ/σ for the *β-trans*, *β-cis*, and α protons, respectively. The plots of the *β-trans* protons were found to be better correlated with σ than those of the remaining two types of protons.

The proton chemical shifts of the PVS, ABz, and St derivatives were examined likewise. The results are given in Table 2, where the correlation coefficients, *r*, and standard deviations, *s*, are listed together with the ρ-values. The α protons of ABz and St derivatives were hardly correlated with σ. The ρ-values for both the *β-trans* and *β-cis* protons were found to decrease in magnitude in the order: PVS>PVE>St>ABz. In Fig. 3, the Hammett plots of the *β-trans* protons for the four types of compounds are shown.

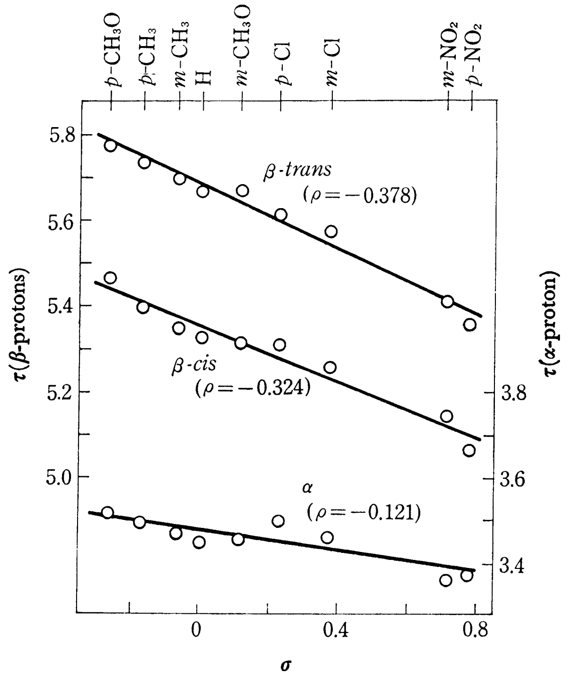


Fig. 2. Hammett plots of the ^{1}H chemical shifts for the ethylenic protons of phenyl vinyl ethers.

Recently, Yamada, Tsuno, and Yukawa[6] succeeded in improving the Hammett-type correlation for the chemical shifts of *m*-substituted aromatic side-chain protons by introducing correction terms for the ring-current diminution by substitution and for the substituent magnetic anisotropy. These corrections do not appear to be important in our *β-trans* protons, probably because they are situated relatively distant from the substituents. Thus, the ρ-values for the *β-trans* protons may be used as a basis for discussing the relative effi-

Table 2. Chemical shifts of aliphatic protons in ring-substituted phenyl vinyl ethers, phenyl vinyl sulfides, allybenzenes and styrenes (in τ)

Substituent X	PVE (-O-)			PVS (-S-)			ABz (-CH$_2$-)			St (-None-)			σ
	α	β_c	β_t	α	β_c	β_t	α	β_c	β_t	α	β_c	β_t	
p-CH$_3$O	3.513	5.467	5.775	3.627	5.015	4.868	4.118	5.030	5.030	3.430	4.501	4.966	−0.268
p-CH$_3$	3.491	5.397	5.736	3.605	4.883	4.818	4.113	5.021	5.024	3.406	4.412	4.905	−0.170
m-CH$_3$	3.468	5.351	5.701	3.549	4.767	4.744	4.110	5.010	5.013	3.400	4.373	4.868	−0.069
H	3.447	5.326	5.670	3.559	4.774	4.747	4.093	5.000	5.001	3.358	4.352	4.842	0
m-CH$_3$O	3.454[a]	5.317	5.671	—	—	—	4.105	4.995	4.985	3.394[a]	4.367	4.846	0.115
p-Cl	3.498	5.303	5.617	3.583	4.728	4.680	4.130	4.934	4.985	3.401	4.363	4.806	0.227
m-Cl	3.456	5.255	5.576	3.542	4.622	4.611	4.119	4.959	4.945	3.403	4.316	4.764	0.373
m-NO$_2$	3.366	5.145	5.414	—	—	—	—	—	—	3.284	4.152	4.602	0.710
p-NO$_2$	3.374	5.067	5.360	3.458	4.377	4.370	—	—	—	—	—	—	0.778
ρ	−0.121	−0.324	−0.378	−0.134	−0.539	−0.448	—	−0.137	−0.126	—	−0.290	−0.335	
r	0.875	0.979	0.988	0.891	0.962	0.987	—	0.895	0.972	—	0.936	0.980	
s	0.025	0.025	0.022	0.031	0.058	0.032	—	0.031	0.014	—	0.045	0.027	

a) Overlappings of α-proton peaks with those of phenyl protons introduced some uncertainty into the obtained values.

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[6] H. Yamada, Y. Tsuno, and Y. Yukawa, This Bulletin, **43**, 1459 (1970).

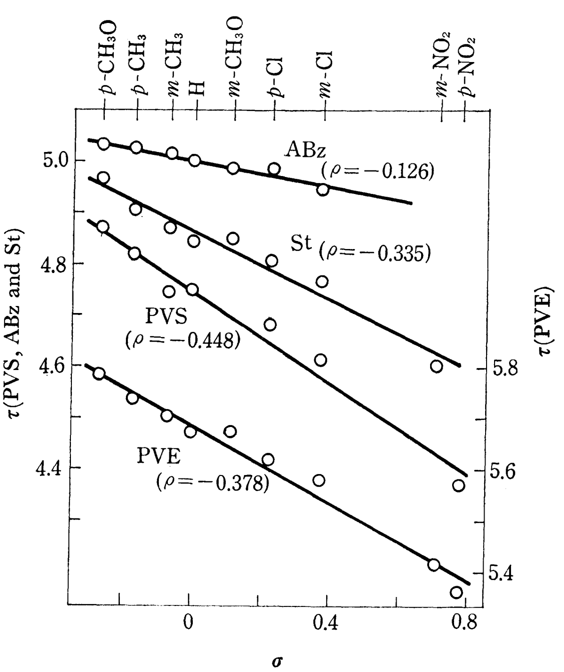

Fig. 3. Hammett plots of the *β-trans* ^1H chemical shifts for phenyl vinyl ethers (PVE), phenyl vinyl sulfides (PVS), allylbenzenes (ABz) and styrenes (St).

ciencies of oxygen, sulfur, and carbon atoms in transmitting the effects of ring substituents to the side chains.

Discussion

(A) Electronic Behavior of Oxygen and Sulfur. The proton chemical shifts and coupling constants of several alkyl vinyl sulfides have recently been reported by Ceccarilli and Chiellini.[7)] Comparing their results with those for oxygen analogs,[8)] they suggested that the decreased shielding of the terminal vinyl protons in the sulfides is due to the electron-accepting conjugation of the sulfur atom. The lower-field shifts of the *β-trans* protons of phenyl vinyl sulfides relative to the ethers (Table 2) can be interpreted in a similar manner.

The chemical shift of a proton bonded to a carbon atom is thought to depend largely on the total electron density at that carbon atom. This view has recently been supported theoretically.[9)] With these points in mind, we may discuss the electronic behavior of the intervening atom or group, Y, in $C_6H_5YCH{=}CH_2$ and $C_6H_5YCH_3$.

The chemical shifts of the side-chain protons in the two types of compounds, where Y is O, S, and CH_2, are compared in Table 3. We see that the τ-values of the β-hydrogens in $C_6H_5YCH{=}CH_2$ decrease in the order: PVE>ABz>PVS, *i.e.* O>CH_2>S. The order changes into CH_2>S>O for the methyl hydrogens in $C_6H_5YCH_3$. Since the electron density of the β-carbon in the vinyl compounds is controlled mainly by the electron-donating or -accepting character of Y through the π-bond, the O>CH_2>S order should be taken to reflect the order of the π-electron-donating ability of these atoms or group. In the same manner, it should be the effect of Y through the σ-bond that determines the electron density of the methyl carbon in $C_6H_5YCH_3$. The observed order of chemical shifts, CH_2>S>O, suggests that the electron-accepting character of Y through the σ-bond increases in the CH_2>S>O order. Therefore, it can be said that oxygen behaves as a π-doner-σ-acceptor, while divalent sulfur acts as a π,σ-acceptor, provided allylbenzene is taken as the standard.

TABLE 3. COMPARISONS OF THE PROTON CHEMICAL SHIFTS

Compound	Proton	Chemical shifts (τ)		
		-O-	-S-	$-CH_3-$
$C_6H_5YCH_3$	methyl	6.34[2)]	7.58[2)]	8.80[10)]
$C_6H_5YCH{=}CH_2$	α	3.45	3.56	4.09
	β-cis	5.33	4.77	5.00
	β-trans	5.67	4.75	5.00

(B) Transmission Efficiency. The ρ-values for the methyl proton in $XC_6H_4YCH_3$ and the *β-trans* protons in $XC_6H_4YCH{=}CH_2$ are summarized in Table 4. Toluene, in which no atom is interposed between the phenyl ring and the methyl group, has a ρ value of -0.214 τ/σ. When a CH_2 group intervenes, ρ decreases in magnitude to -0.113,[10)] about one half the value for toluene. When the CH_2 group is replaced by an oxygen atom, the efficiency of transmission increases to -0.270,[11)] which exceeds in magnitude the corresponding value for toluene. That is to say, the electronic effect is transmitted with amplification under the influence of the oxygen atom. On the contrary, the sulfur atom has no such effect. The ρ value of thioanisole is only -0.115,[2)] nearly equal to that of ethylbenzene. This indicates that, in $XC_6H_4YCH_3$, sulfur is a less efficient transmitter of substituent effects than oxygen.

In $XC_6H_4YCH{=}CH_2$, the transmission efficiency attenuates on going from styrene (-0.335) to allylbenzene (-0.126) and is amplified by the insertion of oxygen

TABLE 4. ρ-VALUES FOR THE CHEMICAL SHIFTS OF TERMINAL PROTONS

Compound	Proton	ρ (τ/σ)			
		-O-	-S-	$-CH_2-$	-None-
$X{-}C_6H_4Y{-}CH_3$	methyl	-0.270[11)]	-0.115[2)]	-0.113[10)]	-0.214[2)]
$X{-}C_6H_4Y{-}CH{=}CH_2$	*β-trans*	-0.378	-0.448	-0.126	-0.335

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7) G. Ceccarilli and E. Chiellini, *Org. Magn. Resonance*, **2**, 409 (1970).

8) H. Yuki, K. Hatada, and M. Takeshita, *J. Polymer. Sci.*, *A-1*, **7**, 667 (1969).

9) O. Kajimoto and T. Fueno, *Chem. Lett.*, **1972**, 103.

10) K. L. Williamson, N. C. Jacobs, and K. T. Soucy, *J. Amer. Chem. Soc.*, **86**, 4021 (1964).

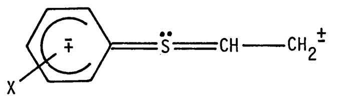
11) C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962).

(−0.378), in just the same manner as in $XC_6H_4YCH_3$. One surprising exception is the enhancement of the transmission efficiency of sulfur; the ρ value (−0.448) of PVS is not only greater than that of styrene but exceeds the value for PVE. This finding can be deemed as the first clear example of a case which supports Marcus' conjecture regarding an enhanced transmission efficiency of sulfur relative to oxygen.[2]

Comparing the transmission efficiencies of sulfur and oxygen, Marcus *et al.*[2] only mentioned that sulfur must be favored over oxygen in situations where the d-orbitals of sulfur can participate in conjugation. In our opinion, however, this reasoning is still rather ambiguous.

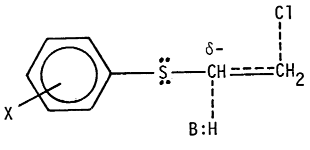
According to Price and Oae,[12] the sulfur atom shows three unique conjugative contributions in addition to the usual electron-donating conjugation common to oxygen and sulfur. Of the three contributions, the electron-accepting and electron-sharing pπ-dπ conjugations play important roles in stabilizing the anionic and radical intermediates. The remaining one is expected to be important when the sulfur atom is placed between two unsaturated groups. This contribution is often referred to as the "through-conjugative" contribution.

As the system examined here has two unsaturated groups directly bonded to the sulfur atom, it seems reasonable to attribute the cause of the enhanced transmission to the through-conjugative contribution of the sulfur atom. That is, the transmission of substituent effects is considered to be enhanced by the contribution of the following canonical structure involving a pπ-dπ-pπ conjugation:



II

In connection with the above argument, recent experimental results by Oae and Yano[13] are of particular interest. They examined the E2-type elimination reaction of β-arylthioethyl chloride kinetically and found that the ρ value for this reaction, 1.98, was greater than that of the oxygen analog, 1.33. As the intermediate suggested for this reaction (III) has a structure similar to that of PVS, it is probable that the "through-conjugative" contribution of the sulfur atom shows up in the transition state. In addition, the reported ratio of reaction constants between sulfur and oxygen derivatives ($\rho_S/\rho_O=1.49$) is a little greater than that observed in our PMR measurements ($\rho_S/\rho_O=1.19$). This suggests that the ρ_S/ρ_O ratio increases with an increase in the anionic character of the system considered.



III

In conclusion, the sulfur atom behaves as a strong transmitter of substituent effects when interposed between two unsaturated groups. This can be interpreted in terms of the "through-conjugation" of the sulfur atom.

The authors are grateful to Mr. Y. Terawaki of this Faculty for his measurements of the proton magnetic resonance spectra and to Professor T. Otsu of Osaka City University for supplying the *p*-nitrophenyl vinyl sulfide.

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

[13] S. Oae and Y. Yano, *Tetrahedron*, **24**, 5721 (1968).