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Electronic Spectra of *O*-Alkyl Thiobenzoates and Their Derivatives

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The absorption spectra of *O*-methyl and -ethyl thiobenzoates and their *p*- and *m*-methoxy, methyl and chloro derivatives have been studied. The substituent effect on the $n \rightarrow \pi^*$ transition of thiocarbonyl group has been discussed with the use of the Hammett relationship.

Among many organic compounds, thiocarbonyl compounds have received little attention until recently. Studies on the electronic spectra of thiocarbonyl compounds are not exceptions. The substituent effect on the spectra of thiobenzophenone was first published by Burawoy and co-workers only with electron-releasing substituents,[1,2] and then by de Boer and co-workers with a variety of substituents.[3] However, some of these compounds are unstable and it is difficult to obtain reliable spectra for the discussion on the substituent effect. *O*-Alkyl thiobenzoates and their derivatives are, on the other hand, stable in air and suitable for spectroscopic studies.

The purpose of this paper is mainly to gather reliable electronic spectral data on *O*-alkyl thiobenzoates and their derivatives and then to discuss the effect of substituents on the electronic transitions of thiocarbonyl group.

Results and Discussion

O-Methyl and -ethyl thiobenzoates and their *p*- and *m*-methoxy, methyl and chloro derivatives were synthesized and subjected to spectrometry.[4] The purity of materials was confirmed by VPC. The spectra were recorded in cyclohexane solution.

The electronic spectra of *O*-alkyl thiobenzoates have two regions of absorption (Fig. 1). The absorption at around 420 mμ is attributable to the $n \rightarrow \pi^*$ transition in the thiocarbonyl group. This characterization is verified by the fact that the intensity of the absorption is low, that a blue-shift of the absorption can be observed on transferring to a more polar solvent ($\lambda_{\max}=418$ mμ, $\varepsilon=98$ in 95% aq. ethanol for *O*-methyl thiobenzoate) and that electron-releasing substituents cause the blue-shift (*vide infra*). The absorption at around 280—290 mμ can be regarded as the $\pi \rightarrow \pi^*$ transition in the arylthiocarbonyl group by the intensities and effects of substituents and solvents ($\lambda_{\max}=288$ mμ, $\varepsilon=9{,}812$ in 95% aq. ethanol for *O*-methyl thiobenzoate). However, since the absorption of this region is accompanied by a shoulder(s) in several compounds, the origin of the transition is not unequivocally assigned. Some of *O*-alkyl thiobenzoates have another absorption at around 230 mμ.

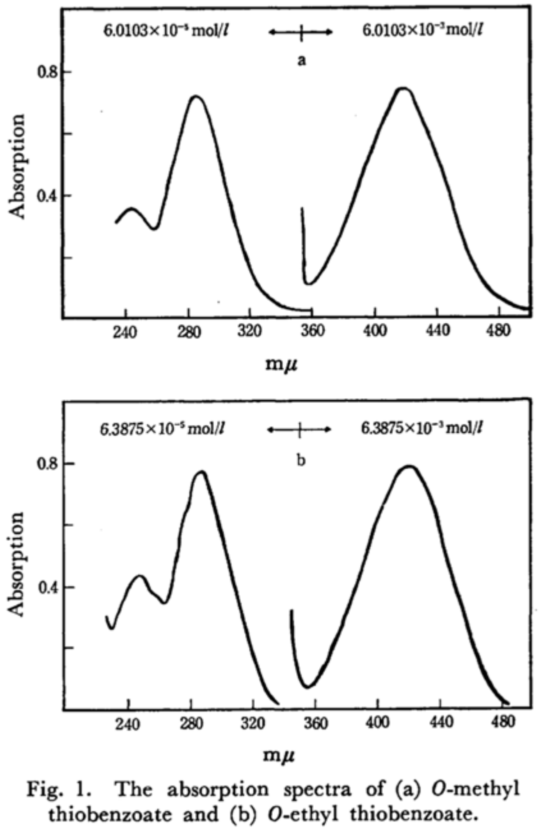

Fig. 1. The absorption spectra of (a) *O*-methyl thiobenzoate and (b) *O*-ethyl thiobenzoate.

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[1] P. Brocklehurst and A. Burawoy, *Tetrahedron*, **10**, 118 (1960).

[2] a) W. A. Lees and A. Burawoy, *ibid.*, **20**, 1527 (1964); b) **20**, 1533 (1964).

[3] a) O. Korver, J. U. Veenland and Th. J. de Boer, *Rec. Trav. Chim. Pays-Bas*, **84**, 289 (1965); b) **84**, 304 (1965).

[4] We thank to Professor S. Inokawa of Sizuoka University for his kind supply of *O*-methyl *p*-nitrothiobenzoate.

TABLE 1. ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS IN THE VISIBLE-LIGHT REGION[a)]

Substituent	Methyl thioester			Ethyl thioester		
	λ, Å	ε	$\Delta\nu$, cm^{-1}	λ, Å	ε	$\Delta\nu$, cm^{-1}
H	4171	121	—	4200	122	—
p-CH_3O	4118	196	+309	4147	208	+304
m-CH_3O	4176	122	−29	4198	121	+11
p-CH_3	4143	134	+162	4188	144	+68
m-CH_3	4165	128	+35	4188	132	+68
p-Cl	4215	120	−250	4221	141	−119
m-Cl	4200	110	−165	4241		−231
p-NO_2	4329	177	−875	—	—	—

a) In cyclohexane.

TABLE 2. ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS IN THE ULTRAVIOLET REGION[a)]

Substituent	Methyl thioester		Ethyl thioester	
	λ, Å	ε	λ, Å	ε
H	2871	11647	2879	12211
	2465	5907	2476	7076
p-CH_3O	3112	21853	3118	17873
	2577	5352	2606	4830
m-CH_3O	3200	shoulder	3182	shoulder
	2867	10671	2879	11049
p-CH_3	2941	13401	2953	14897
	2465	5430	2524	6728
m-CH_3	2882	14297	2882	12832
	2588	6068	2588	6117
	2493	6035	2506	6150
p-Cl	2918	12921	2929	13890
	2481	7613	2553	7610
m-Cl	3193	shoulder	2929	shoulder
	2828	11763	2847	10090
	2624	shoulder	2588	5814
p-NO_2	2988	11196	—	—

a) In cyclohexane.

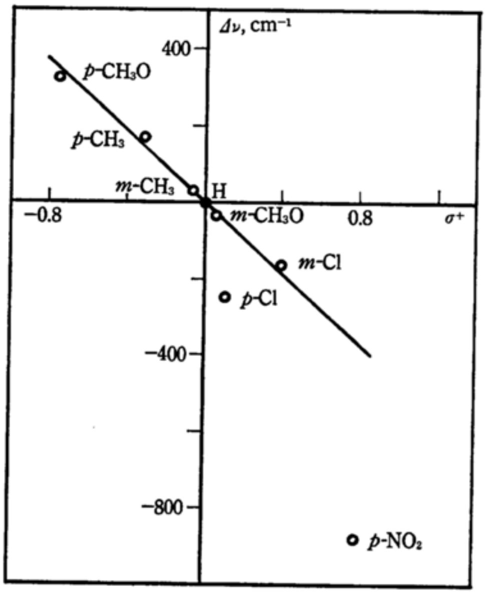


Fig. 2. Hammett relationship for the $n\rightarrow\pi^*$ transition of *O*-methyl thiobenzoates.

This is probably due to the interaction between the substituent and the phenyl-ring. The absorption maxima and the molar extinction coefficients are listed in Tables 1 and 2. In Table 1, the shifts in wave numbers of thiocarbonyl absorption band of substituted *O*-alkyl thiobenzoates relative to the corresponding unsubstituted thioesters are also listed.

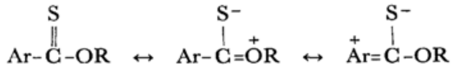
A remarkable substituent effect can be observed in the $n\rightarrow\pi^*$ transition: the Hammett plot, according to the equation.

$$\Delta\nu = \nu_X - \nu_H = \rho\sigma^+$$

is shown in Fig. 2 for the $n\rightarrow\pi^*$ transition of *O*-methyl thioesters. The *O*-ethyl thioesters behave similarly.

Obviously, electron-withdrawing substituents at the *p*-position exert different effect from the others on the transition. Let us assume that this is due to larger conjugative effect of such substituents in the n, π^* excited state of the thioester than in its ground state.

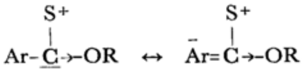
It will be interesting to compare the substituent effect in the thioester and that in thiobenzophenone or in 2,4,6-trimethylthiobenzophenone, where electron-releasing and -withdrawing substituents each give lines with different slopes regardless the position of substituents.[3a)] In series of substituted thiobenzophenones, it has been assumed that, as a consequence of an electronic influence by an electron-withdrawing substituent in *p*-position, the phenyl or even the 2,4,6-trimethylphenyl group reaches a greater degree of coplanarity with the thiocarbonyl group than the *p*-substituted phenyl group. Therefore, only the inductive effect of the substituent can act upon the transition. Thus, there exists a distinct difference in the conjugative effects of electron-withdrawing substituents between thioesters and thiobenzophenones. This difference might be interpreted as follows: since



$\mathrm{Ar{-}\overset{\overset{S}{\|}}{C}{-}OR} \leftrightarrow \mathrm{Ar{-}\overset{\overset{S^-}{|}}{C}{=}\overset{+}{O}R} \leftrightarrow \mathrm{\overset{+}{Ar}{=}\overset{\overset{S^-}{|}}{C}{-}OR}$

(**1a**) (**1b**) (**1c**)

the thiocarbonyl group is highly polarized in its ground state,[5-7] the contribution of the structure **1b** is fairly important in the ground state of the thioester.[7] On the other hand, since the polarization of the thiocarbonyl group is reverse in the *n*, π^* exited state[8] to that in the ground state, the resonance effect of the oxygen atom no more operates. As a consequence, the importance of the structure (**2b**) increases in the *n*, π^* excited state.



$\mathrm{Ar{-}\underline{\overset{\overset{S^+}{|}}{C}}{\to}OR} \leftrightarrow \mathrm{\overset{-}{Ar}{=}\overset{\overset{S^+}{|}}{C}{\to}OR}$

(**2a**) (**2b**)

Although the limited number of substituents do not allow to estimate the relative importance of the resonance effect quantitatively, the present results show that electron-releasing substituents can conjugate with the thiocarbonyl group in the ground state, whereas electron-withdrawing substituents interact with the thiocarbonyl group in the *n*, π^* excited state. It should be noted that the phenyl group in thiobenzophenone or the mesityl group in 2,4,6-trimethylthiobenzophenone has ability to conjugate with the thiocarbonyl group both electron-releasingly and -withdrawingly.

Unfortunately, the susceptibility of the substituent effect to the thiocarbonyl group cannot be compared with that to the carbonyl group, because the absorption due to the $n \to \pi^*$ transition in benzoates are completely hidden by an intense band of the $\pi \to \pi^*$ transition.

For the $\pi \to \pi^*$ transition, the difference of absorption maxima between *p*- and *m*-positions for each substituents correlates well to the value of $\Delta\sigma = \sigma_p - \sigma_m$. This fact indicates that the absorption in this region is largely affected by a resonance effect of substituents.[9] The plot is shown in Fig. 3 for the *O*-methyl thioesters. The linear correlations of $\Delta\nu$ with σ and σ_R is also found for *m*- and *p*-substituted thioesters, except for the *p*-nitro derivative, respectively, as has been found for the system of 2,4,6-trimethylthiobenzophenone.[3a]

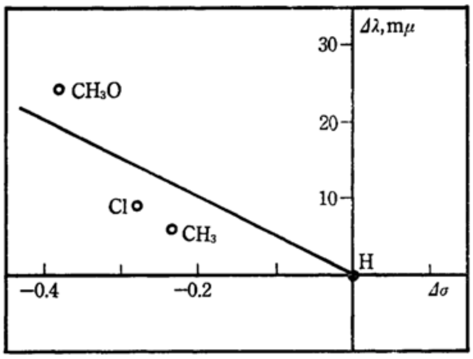


Fig. 3. The correlation of $\Delta\lambda$ *vs.* $\Delta\sigma$ for the $\pi \to \pi^*$ transition of *O*-methyl thiobenzoates.

Experimental

Materials. As previously reported,[10] the thioesters were prepared from the corresponding orthoesters[11] or from the corresponding imido ethers.[12,13] The purities were confirmed by IR, NMR and VPC. The results of elemental analyses were satisfactory for each compound.

Spectrometry. Spectra were obtained on a Cary-14 Spectrophotometer using spectrograde cyclohexane as solvents. The concentrations of solutions were adjusted so as to obtain the spectra, in which the maxima of a band had around 70—80% absorption. These were 6×10^{-3} M for visible and 6×10^{-5} M for UV revion, respectively. The estimated error in wavelength is ±1 mμ.

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