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Substituent Effect on Carbonyl and Carboxylate Stretching Frequencies of Phenacyl Benzoates

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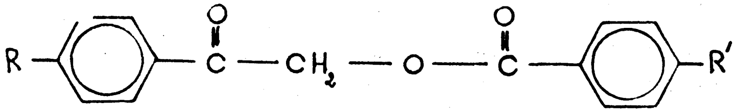
In the present communication, the substituent effects on carbonyl and carboxylate stretching frequencies of phenacyl benzoates have been studied.

INTRODUCTION

The positions and integrated absorption intensities of the carbonyl and carboxylate stretching bands in the infrared spectra of phenacyl benzoates with substitution in benzoic acid or acetophenone moiety have been measured in benzene solution. The vartiation of these quantities is discussed in relation to the nature of the substituent group.

The kinetics of the reaction of phenacyl bromide with benzoic acid in the presence of triethylamine have been studied extensively and the correlation of rate constants with substituent constants is found to be linear[1]. The correlation of carbonyl or carboxylate stretching bands with substituent constants has been carried out for acetophenones[2], ethyl benzoates[3] and benzoic acids[4] and a linear relationship is observed; this indicates that the same combination of factors that control the chemical reactivity of these compounds are responsible for the shift in their carbonyl and carboxylate stretching bands.



Structure I

Phynacyl benzoates(I) contain both acetophenone and ethyl benzoate moieties. So, a linear free energy relationship is expected between the substituent constant and the structure sensitive ketonic ν(C=O) and acid ν_{as} (COO). Therefore, in the present work the effect of substituent on these frequencies and their absorption intensities is examined with a view to check the applicability of Hammett type relationships.

The *p*-substituted phenacyl benzoates were prepared by reacting *p*-substituted phenacyl bromides with benzoic acid in the presence of triethylamine and the phenacyl-4-substituted benzoates by reacting phenacyl bromide with *p*-substituted benzoic acids as described in literature[5-7]. Their purities were checked by their melting points and TLC. The infrared spectra were taken on a Shimadzu IR-435 infrared spectrophotometer with polystyrene as the internal standard. In the region 1800–1650 cm^{-1} the spectra were taken in benzene (0.1 M) with four times expansion using a 0.01 cm cell.

Correlation of frequency with substituent constant

The carboxylate stretching band, $\nu_{as}(COO)$ appear in the region 1725–1740 cm^{-1} (Table 1). The correlation of $\nu_{as}(COO)$ with Hammett substituent constant, σ gave a correlation coefficient of 0.972. But, the correlation of $\nu_{as}(COO)$ with electrophilic substituent constant, σ_p^+ gave a better fit with a correlation coefficient of 0.996, indicating that there is extensive conjugation in phenacyl benzoates compared to benzoic acid system. Correlation of $\nu_{as}^2(COO)$ with σ_p^+ shows that there is a linear relation between the bond force constant and the square of frequency, as expected from Hooke's equation.

TABLE 1
$\nu(C=O)$ AND $\nu_{as}(COO)$ BANDS (cm^{-1}) FOR PHENACYL BENZOATES IN BENZENE (0.1 M SOLUTION)

Substituents		$\nu(C=O)$	$\nu_{as}(COO)$
R	R′		
OCH_3	H	1684	1731
CH_3	H	1703	1731
H	H	1707	1731
Cl	H	1708	1731
Br	H	1707	1731
NO_2	H	1713	1731
H	OCH_3	1707	1725
H	CH_3	1707	1728
H	F	1707	1731
H	Cl	1707	1732
H	I	1707	1733
H	NO_2	1707	1738

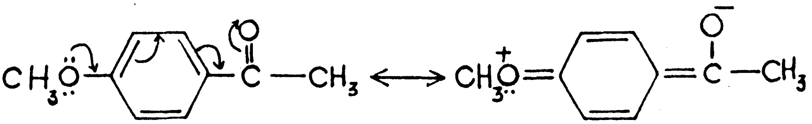
The plot of log $\nu_{as}(COO)$ vs σ_p^+ is also linear with a correlation coefficient of 0.993. From the above results, it is concluded that the best fit is given by the linear relation, (Fig. 1).

$$\nu = 1731.2 + 8.4\,\sigma_p^+ \qquad (1)$$

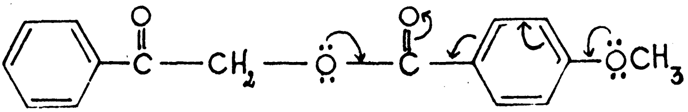
The carbonyl stretching bands of the phenacyl benzoates were observed between 1715 and 1680 cm^{-1} (Table 1). Similar to $\nu_{as}(COO)$, the correlation of $\nu(C=O)$, $\nu^2(C=O)$ and log $\nu(C=O)$ with substituent constant were made and the best relationship is given by the equation, (Fig. 2).

$$\nu = 1706.3 + 8.7\sigma_p^+ \tag{2}$$

The *p*-methoxy substituent deviates much from the linearity shown by all other substituents. This may be due to the more extensive conjugation (II) than expected normally for the methoxy group. Similar anomolous deviation has been observed previously[8] for the basicities of acetophenones.



Structure II



Structure III

However, a similar effect is not observed for $\nu_{as}(COO)$ because of cross-conjugation of C=O with C-O in the carboxylate group (III).

The multiple correlation of carboxylate stretching band with σ_I and σ_R^+ shows the better correlation that the inductive effect slightly predominates over resonance effect.

$$\rho_I = 9.56\ cm^{-1},\ \rho_R = 7.93\ cm^{-1} \text{ and } R = 0.999$$

Correlation of Intensity with substituent Constant

The integrated band intensity (A) for carbonyl and carboxylate stretching bands were calculated using the equation[9],

$$A = K(1/Cl)\log(T_0/T_{max}) \times 2.303 \times 10^{-4}\ mol^{-1}\ lit\ cm^{-2}$$

where C is concentration in moles per litre

l is cell length in cm

log (T_0/T_{max}) is optical density at the absorption maximum

$\Delta\nu_{1/2}$ is band intensity in cm^{-1} at half maximal intensity

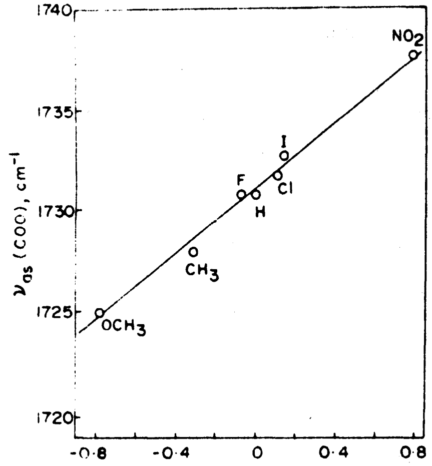


Fig. 1 Plot of $\nu_{as}(COO)$ vs σ_p^+

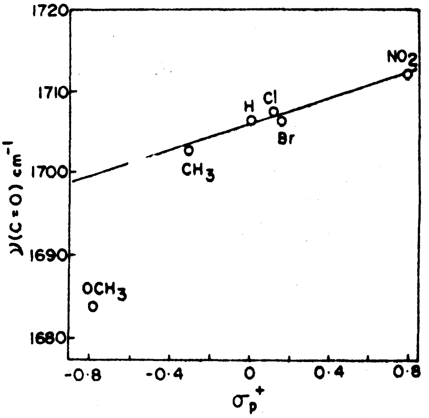


Fig. 2 Plot of $\nu(C{=}O)$ vs σ_p^+

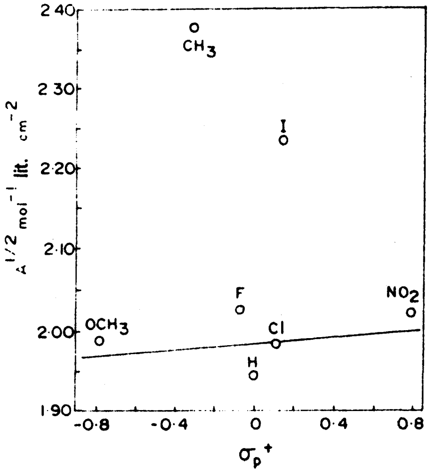


Fig. 3 Plot of $A^{1/2}$ vs σ_p^+ for carboxylate stretching frequency

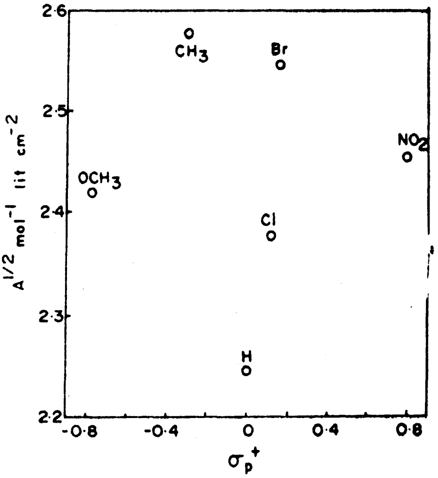


Fig. 4 Plot of $A^{1/2}$ vs σ_p^+ for carbonyl stretching frequency

K is a constant dependent on the ratio $S'/\Delta\nu_{1/2}$

S' is slit width (0.072 cm)

The correlation of log A and $A^{1/2}$ of carboxylate stretching band with substituent constant (σ and σ^+) is very poor (Fig. 3). Thus, the effect of substituent on the carboxylate band intensity is very low. This is due to the fact that the band intensity is determined by the resonance effect alone and band position by combined resonance and inductive effect[10]. Similarly for carbonyl band intensity a scattergram (Fig. 4) is obtained. This shows that there is no correlation between carbonyl band intensity and substituent constant.

On the basis of the above discussion it is concluded that the LFER is most applicable to $\nu_{as}(COO)$ rather than to $\nu(C{=}O)$. The effect of substituents on both the carboxylate and carbonyl band intensities is very small.

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