

Correlation of ground and excited state dissociation constants of *trans*-*para*- and *ortho*-substituted cinnamic acids

R MURUGESAN, BRAJASEKAR, T LEKSHMANA THANULINGAM
and A SHUNMUGASUNDARAM*

Department of Chemistry, VHNSN College, Virudhunagar 626001, India

MS received 8 November 1991; revised 17 February 1992

Abstract. The ground and excited state dissociation constants of *trans*-*para*- and *ortho*-substituted cinnamic acids have been determined in 50% (v/v) dioxan–water mixture at 30°C using the Forster cycle. The measured dissociation constants are analysed in the light of single and dual substituent parameter (DSP) equations. Excited state dissociation constants of *p*-substituted cinnamic acids correlate well with the exalted substituent constants. The DSP method of analysis shows that resonance effect is predominant relative to inductive effect in the excited state than in the ground state for the *para*-substituted acids. The single parameter equation gives poor correlation for the *ortho*-substituted acids. However, the DSP analysis shows fairly good correlation. The inductive effect is predominant relative to the resonance effect in the excited state than in the ground state.

Keywords. Ground and excited state dissociation constants; cinnamic acids; substituent effects; dual substituent parameter analysis.

1. Introduction

Acid–base equilibrium reactions of aromatic compounds and the influence of substituents in the ground electronic state have been given much attention (Jones and Hancock 1960; Chapman and Shorter 1978). Although the chemistry of the excited state is of wide interest (Jaffe' and Jones 1965; Kolanchi Babu *et al* 1986), considerably less attention has been paid towards the substituent effect on electronically excited acid–base properties. Photochemical studies (Havinga *et al* 1956; Zimmerman and Sandel 1963) indicated that substituent effects in electronically excited states may not always be predictable from the ground state chemical behaviour. Since the charge densities are often modified by electronic excitation, it can be expected that the acid–base properties of a molecule in an excited state will also differ from its properties in the ground state. A number of investigators are deeply studying the mechanisms of reactions occurring in the excited states. The pioneering research of Forster (1950) and Weller (1961) paved the way for the measurement of chemical equilibrium between the molecules in their excited states, in particular, of acid–base equilibrium. In the present study, we report our investigations on ground and excited state properties of *trans*-*para*- and *ortho*-substituted cinnamic acids. The acid–base equilibrium constants in ground and singlet excited state have been analysed with single parameter and dual substituent parameter (DSP) equations in order to understand the electronic substituent effect in both ground and excited states.

2. Materials and methods

All the *trans*-*para*- and *ortho*-substituted cinnamic acids were prepared by the literature methods (Anderson and Wang 1954; Beech 1954; Compaigne and Meyer 1962). The solvent dioxan was purified by the literature method (Weisburger and Proskumar 1955). The ground state dissociation constant determination of the cinnamic acid and substituted cinnamic acids in 50% (v/v) dioxan–water mixture was done by the spectrophotometric method (Cohen and Jones 1963). The electronic absorptions in acids, alkaline and sodium chloride solutions were recorded from 200–360 nm on a Hitachi model 200–20 spectrometer. The dissociation constants were calculated according to the equation,

$$pK_a = \text{pH} + \log \frac{(b - \varepsilon)}{(\varepsilon - a)}, \quad (1)$$

where a is the optical density of solution of cinnamic acids at a given wavelength, b is the optical density of the corresponding cinnamate anion at the same wavelength and ε is the optical density in sodium chloride medium. The pH values of the solutions were determined using Elico pH meter. The excited state dissociation constants were calculated by employing the Forster cycle (Jaffe' *et al* 1964), using the equation

$$pK_a - pK_a^* = \frac{hc(\bar{\nu}_{\text{HA}} - \bar{\nu}_{\text{A}^-})}{2.303 RT} \quad (2)$$

where $\bar{\nu}_{\text{HA}}$ and $\bar{\nu}_{\text{A}^-}$ represent frequency of the lowest absorption bands of acid and conjugate base and pK_a and pK_a^* are the ground and excited state dissociation constants.

3. Results and discussions

The spectroscopic results are summarised in table 1. It has been shown that the *para*- and *ortho*-substituted acids exhibit a hypsochromic shift when the solvent medium is changed from acidic to basic. It is interesting to note the anomalous behaviour of *p*-nitrocinnamic acid. As compared to other substituents the shift is towards the longer wavelength for the nitro group. However, this type of anomalous behaviour of nitro group is well-known in other series too (Doub and Vandenbelt 1947). The nitro group itself is capable of intense absorption in this region. Hence the optical spectrum of nitro substituted acid becomes more complex. From the table 1 it is seen that electron-attracting substituents decrease the pK_a values and electron-releasing substituents increase it. When the ground and excited state dissociation constants are compared, the cinnamic acids containing electron-releasing substituents show less acidic character in their excited state than their ground state. The *p*-nitrocinnamic acid becomes very strongly acidic in the excited state.

The ground and excited state dissociation constants of substituted acids have been correlated with various Hammett substituent constants. The difference between absorption frequency of substituted acid and its conjugate base, $\Delta\bar{\nu}$ is also correlated with the substituent constants. The results of statistical analysis are collected in table 2.

Table 1. Absorption maxima, ground and excited state dissociation constants of *trans*-para and ortho-substituted cinnamic acids.

Substituent	HA λ_{\max} (nm)	A ⁻ λ_{\max} (nm)	$\Delta\bar{\nu}$ (cm ⁻¹)	pK_a	pK_a^*
<i>p</i> -OMe	309	284	-2850	5.986	11.65
<i>p</i> -Me	286	274	-1531	5.883	9.020
<i>p</i> -H	277	268	-1212	5.627	8.104
<i>p</i> -F	276	266	-1212	5.627	8.104
<i>p</i> -Cl	282	272	-1304	5.536	8.219
<i>p</i> -Br	284	274	-1282	5.523	8.163
<i>p</i> -NO ₂	306	316	1033	5.125	2.953
<i>o</i> -OMe	325	311	-1078	6.037	8.263
<i>o</i> -Me	278	269	-1204	5.697	8.143
<i>o</i> -F	270	262	-1130	5.621	7.953
<i>o</i> -Cl	274	268	-817	5.540	7.226
<i>o</i> -Br	274	267	-957	5.577	7.522

Table 2. Statistical correlation of pK_a , $\Delta\bar{\nu}$ and pK_a^* of *trans*-para and ortho-substituted cinnamic acids.

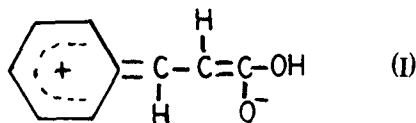
System	Quantity correlated	Substituent constant	Correlation coefficient	Slope	Standard deviation
<i>p</i> -Substituted cinnamic acid	pK_a	σ_p	0.973	-0.479	0.053
<i>o</i> -Substituted cinnamic acid	pK_a	σ_o	0.897	-0.641	0.092
<i>p</i> -Substituted cinnamic acid	$\Delta\bar{\nu}$	σ_p	0.855	-0.756	0.104
		σ_p^\ddagger	0.931	3089	459
<i>p</i> -Substituted cinnamic acid	pK_a^*	σ_p	0.984	1832	224
		σ_p^\ddagger	0.944	-7.07	0.934
<i>o</i> -Substituted cinnamic acid	pK_a^*	σ_o	0.989	-4.16	0.403
		σ_o	0.733	-1.16	0.306
		σ_p	0.894	-1.75	0.201
		σ_p^+	0.729	-0.839	0.308

A satisfactory correlation is obtained for the ground state dissociation constant of *p*-substituted cinnamic acids with the Hammett substituent constants. The correlation between $\Delta\bar{\nu}$ and the substituent constants is fairly good for *p*-substituted acids.

According to the Forster cycle the $\Delta\bar{\nu}$ is proportional to the difference, $\Delta pK_a = pK_a^* - pK_a$. Since the ground state pK_a values correlate with the Hammett substituent constants, it follows that the same is true for pK_a^* . The excited state dissociation constants of *p*-substituted acids give fairly good correlation when the σ_p constants are used. The excited state ρ value (-7.07) is significantly larger than the one in the ground state (-0.478) for the *p*-substituted acids. The higher value of ρ in the excited state implies a very strong interaction between the substituent and acidic centre. The negative slope in the above correlation indicates that the dissociation constants (pK_a) increase with electron-releasing substituents.

The effect of substituents on the excited state dissociation constant can be explained by valence bond theory (Bastrop and Coyle 1975; Srinivasan 1986). In aromatic carboxylic acids excitation to the S_1 state causes the charge migration away from the

ring. This can be represented by an increased contribution of the resonance structure of the type shown in I.



The net effect is to reduce the acidity of the S_1 state of aromatic carboxylic acids. The pK_a values of S_1 state of cinnamic acids given in table 1 are in agreement with this prediction. Further the results of statistical analysis reveal that for the p -substituted cinnamic acids the exalted sigma (σ_p^\pm) constants give a better correlation than the σ_p constants with pK_a^* and $\Delta\bar{\nu}$ values. This fact supports the importance of resonance effect in the excited state.

In order to understand the relative contribution of resonance and inductive effect of p -substituents, we have attempted to analyse the data by the DSP equation

$$pK_a = \alpha\sigma_I + \beta\sigma_R + h. \quad (3)$$

The results of the DSP analysis obtained may be expressed by (4) and (5) for ground and excited states respectively.

$$pK_{a\text{para}} = -0.766\sigma_I - 0.833\sigma_R + 5.688 \quad (4)$$

$$\pm 0.083 \quad \pm 0.090$$

$$R = 0.988; \quad SE = 0.054; \quad F = 78.9; \quad n = 7; \quad CL > 99.5\%$$

$$pK_{a\text{para}}^* = -5.77\sigma_I - 8.66\sigma_R + 8.02 \quad (5)$$

$$\pm 1.18 \quad \pm 1.28$$

$$R = 0.970; \quad SE = 0.762; \quad F = 32.3; \quad n = 7; \quad CL > 99.5\%$$

In the correlation, R = multiple correlation coefficient; SE = standard error of estimate; F = value of F -test; n = number of data points; CL = confidence level. The correlations are all meaningful since the confidence levels of the F -test are greater than 95%. The standard errors of estimate are low. The confidence levels for the significance of Student t test are above 90% (Aslam *et al* 1981). It is of interest to consider the variation of the composition of electronic effects (Charton 1975; Civetanovic *et al* 1979) of the substituents. For this purpose the parameter P_R is used and it is defined by the following equation

$$P_R = \frac{|\beta/100|}{|\alpha| + |\beta|}. \quad (6)$$

The P_R values are computed to be 52.1 for ground state and 60.0 for excited state dissociation constants. These values indicate that the contribution of resonance effect is greater than the inductive effect. Further, the magnitudes of P_R values indicate that for excited p -substituted compounds the important mode of transmission of electronic effect of the substituent is resonance. The resonance effect has increased to

an extent of 10 times in the excited state than in the ground state. But the inductive effect is increased only to an extent of 7.5 times in the excited state than in the ground state. The observed trend in the excited state acidities of para-substituted compounds suggests that the resonance effect of substituents far outweighs the inductive effect in the excited state.

Both the ground and excited states of *o*-substituted cinnamic acids do not correlate well with the single parameter equations. Since the single parameter equation did not yield satisfactory correlation, the dissociation constants of *o*-substituted acids were analysed using the DSP equation. The results of the regression analysis obtained for the ground and excited states can be expressed in the following equations (7) and (8) respectively.

$$pK_{a\text{ortho}} = -0.664\sigma_I - 0.975\sigma_R + 5.60 \quad (7)$$

$$\pm 0.180 \quad \pm 0.206$$

$$R = 0.941; \quad SE = 0.079; \quad F = 11.7; \quad n = 6; \quad CL = 99.5\%$$

$$pK_{a\text{ortho}}^* = -1.84\sigma_I - 1.58\sigma_R + 7.96 \quad (8)$$

$$\pm 0.52 \quad \pm 0.60$$

$$R = 0.900; \quad SE = 0.229; \quad F = 6.38; \quad n = 6; \quad CL > 95\%.$$

The correlation obtained in the DSP analysis is better than the single parameter method for the *o*-substituted acids. The correlation was also performed with the three parameter equation (9) involving localised, delocalised and steric terms.

$$pK_{a\text{ortho}} = \alpha\sigma_I + \beta\sigma_R + \phi v + h \quad (9)$$

The results of the regression equation (9) may be expressed by

$$pK_{a\text{ortho}} = -0.669\sigma_I - 0.976\sigma_R + 0.012v + 5.59 \quad (10)$$

$$\pm 0.239 \quad \pm 0.253 \quad \pm 0.202$$

$$R = 0.942; \quad SE = 0.097; \quad F = 5.20; \quad n = 6; \quad CL > 95\%.$$

$$pK_{a\text{ortho}}^* = -1.59\sigma_I - 1.52\sigma_R - 0.553v + 8.12 \quad (11)$$

$$\pm 0.52 \quad \pm 0.55 \quad \pm 0.437$$

$$R = 0.946; \quad SE = 0.209; \quad F = 5.64; \quad n = 6; \quad CL > 95\%.$$

The significance of the various contributing terms was tested by means of the *t*-test. The confidence levels of the *t*-test for the significance of the localised and delocalised terms are above 90% and that of the steric term is below 90% indicating that localised and delocalised effects are important in this series. The analysis with three parameter equation does not show appreciable improvement over the two parameter equation. Therefore it appears that some other factors other than localised and delocalised effects are also operating in the *o*-substituted compounds.

From the analysis, it appears that in the ground state the resonance effect is higher than the inductive effect and in the excited state the contribution of inductive effect is slightly greater than the resonance effect. Thus when the ground and excited states of *o*-substituted acids are compared, the resonance effect has not significantly increased

as in the case of *p*-substituted compounds. In this case, the inductive effect is increased to an extent of 3 times in the excited state than in the ground state. But the resonance effect has increased by only about 1.5 times in the excited state.

Acknowledgements

We thank the Managing Board, VHNSN College, Virudhunagar for encouragement.

References

- Anderson A G and Wang S Y 1954 *J. Org. Chem.* **19** 277
Aslam M H, Burden A G, Chapman N B, Shorter J and Charton M 1981 *J. Chem. Soc., Perkin Trans. 2* 500
Bastrop J A and Coyle J D 1975 *Excited state in organic chemistry* (New York: John Wiley)
Beech W F 1954 *J. Chem. Soc.* 1297
Campaigne E and Meyer W W 1962 *J. Org. Chem.* **27** 2835
Chapman N B and Shorter J 1978 *Correlation analysis in chemistry – recent advances* (New York: Plenum) p. 189
Charton M 1975 *J. Org. Chem.* **40** 407
Civitanovic R J, Singleton D L and Parakevopoulos G 1979 *J. Phys. Chem.* **83** 50
Cohen L A and Jones W M 1963 *J. Am. Chem. Soc.* **85** 3402
Doub L and Vandenberg J M 1947 *J. Am. Chem. Soc.* **69** 2714
Forster T 1950 *Z. Elektro. Chem.* **54** 42
Havinga E, Jongh R O and Dorst W 1956 *Recl. Trav. Chim.* **75** 378
Jaffe' H H, Beveridge D L and Jones H L 1964 *J. Am. Chem. Soc.* **86** 2932
Jaffe' H H and Jones H L 1965 *J. Org. Chem.* **30** 964
Jones L A and Hancock C K 1960 *J. Org. Chem.* **25** 226
Kolanchi Babu M, Rajasekaran K, Kannan N and Gnanasekaran C 1986 *J. Chem. Soc., Perkin Trans. 2* 1721
Srinivasan C 1986 *Chem. Educ.* **2** 28
Weisburger A and Proskumar S 1955 *Organic solvents* (New York: Interscience) p. 371
Weller A 1961 *Progress in reaction kinetics* (ed.) G Porter (New York: Pergamon) Vol. 1, p. 187
Zimmerman H E and Sandel V R 1963 *J. Am. Chem. Soc.* **85** 915