TRANSMISSION OF SUBSTITUENT EFFECTS

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Abstract

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TRANSMISSION OF SUBSTITUENT EFFECTS

IN THE SERIES OF CIS- AND TRANS-CINNAMIC ACIDS

The aim of the present work was to clarify the question of whether the effect of substituents is transmitted equally effectively to the reaction center in the series of cis- and trans-cinnamic acids. Although this problem has been studied previously ([1,2]), the results of the investigations are contradictory and do not give a definite answer to the question posed.

$$X{-}C_6H_4{-}CH{=}CHCOOH$$

For the study we used the method of comparing the constants ρ of the Hammett equation

$$\lg(K/K_0) = \sigma\rho.$$

According to Jaffé ([3]), ρ depends on three factors: 1) the effectiveness with which the electronic effect of the substituent is transmitted to the reaction center, 2) the sensitivity of the given reaction to changes in electron density at the reaction center, and 3) the reaction conditions. Consequently, for a given type of reaction carried out under identical conditions, for reaction series I and II, differing only in the transmitting systems, the value of ρ will be determined only by the effectiveness of transmission of the substituent effect to the reaction center Y.

$$X{-}C_6H_4{-}Y \quad (I) \qquad X{-}C_6H_4{-}A{-}Y \quad (II)$$

Thus, comparison of the values of ρ makes it possible to give a quantitative assessment of the transmission of substituent effects by different systems.

We determined potentiometrically the dissociation constants of substituted cis- and trans-cinnamic and benzoic acids in 49% (by weight) ethanol at 25° (see Table 1). The determinations were carried out on an LP-58 pH meter with glass and calomel electrodes. Using σ from the table of McDaniel and Brown ([5]), we calculated the values of ρ. It was found that for the series of trans-cinnamic acids $\rho_{\text{trans}} = 0.73 \pm 0.05$; $r = 0.990$. For the series of cis-cinnamic acids $\rho_{\text{cis}} = 0.57 \pm 0.04$; $r = 0.983$. For the series of benzoic acids $\rho_{\text{benz}} = 1.35 \pm 0.06$; $r = 0.995$ (r is the correlation coefficient).

From comparison of the constants ρ for the first two series of acids it follows that the double bond conjugated with the benzene ring transmits the effect of substituents somewhat better in the case of the trans isomer than in the case of the cis isomer. Since the difference between ρ_{trans} and ρ_{cis} is small, we carried out a statistical analysis of the results obtained ([12]) and showed that this difference is statistically significant.

It is interesting to note that the conclusion made in the present work concerning the more effective transmission of substituent effects in the series of trans-cinnamic acids, as compared with the cis series, is in agreement with the result obtained by Blomfeld and Fuchs ([1]) in studying the hydrolysis of esters of substituted cis- and trans-cinnamic acids. At the same time, the value found by us

the ratio $\rho_{\text{cis}}/\rho_{\text{trans}} = 0.78$ for acid dissociation is close to the value $\rho_{\text{cis}}/\rho_{\text{trans}} = 0.85$ for ester hydrolysis.

However, our data are at variance with the conclusion of Džakubauskas (2), who also studied the transmission of substituent effects to dissociation constants in a series of cis-cinnamic acids. Having determined ρ only for a series of cis-cinnamic acids, $\rho_{\text{cis}} = 0.498 \pm 0.021$ (in water), and compared it with the value $\rho_{\text{trans}} = 0.466 \pm 0.040$, calculated by Jaffé (3), Džakubauskas concluded that the transmission of substituent effects in the cis and trans isomers of cinnamic acids is the same within experimental error.

Table 1

Dissociation constants of substituted benzoic, trans-cinnamic, and cis-cinnamic acids in 49% (by weight) ethanol at 25 °C

Substituent	Benzoic-acid series, m.p., °C	Benzoic-acid series, $K \cdot 10^6$	trans-Cinnamic-acid series, m.p., °C	trans-Cinnamic-acid series, $K \cdot 10^6$	cis-Cinnamic-acid series, m.p., °C	cis-Cinnamic-acid series, $K \cdot 10^6$
H	123.5–124.5	1.25 ± 0.15	135.2–135.7	1.05 ± 0.18	67.0–68.0	2.79 ± 0.41
n-NO_2	240.0–241.0	14.0 ± 0.2	–	–	–	–

Substituent	Benzoic-acid series, m.p., °C	Benzoic-acid series, $K \cdot 10^6$	trans-Cinnamic-acid series, m.p., °C	trans-Cinnamic-acid series, $K \cdot 10^6$	cis-Cinnamic-acid series, m.p., °C	cis-Cinnamic-acid series, $K \cdot 10^6$
m-NO_2	139.5—140.7	13.7±0.9	205.0—206.0	3.82 ± 0.42	159.0—159.5	6.40 ± 0.40
n-Cl	240.0—241.0	2.38 ± 0.04	249.5—249.8	2.00 ± 0.14	112.8—114.0	4.09 ± 0.09
n-Br	255.5—256.0	3.65 ± 0.11	264.7—265.5	1.92 ± 0.21	127.6—128.5	4.02 ± 0.24
n-CH_3O	184.1—185.4	0.68 ± 0.03	188.0—188.2	0.70 ± 0.02	68.8—69.7	1.78 ± 0.10
n-NH_2	188.5—188.9	0.17 ± 0.01	—	—	—	—
n-$(CH_3)_2N$	—	—	118.0—120.0	0.32 ± 0.03	—	—

For a quantitative assessment of the transmission of substituent effects by different systems, it is most appropriate to compare relative ρ values, calculated by division by the value of ρ for the same reaction in the benzene series. Relative ρ values depend neither on the type of reaction nor on the conditions under which it is carried out.

Table 2 gives the relative ρ values characterizing the transmission of substituent effects through a double bond conjugated with the benzene ring in the case of the cis and trans isomers.

Table 2

Values of $\rho_{relative}$

Reaction	ρ_{trans}	ρ_{cis}
Hydrolysis of esters of cinnamic acids	0.532 (7)0.540 **	0.461 **
Dissociation of cinnamic acids	0.466 (3)0.539 *	0.643 (4)0.498 (2)0.422 *
Reaction of isotopic exchange of hydrogen of ketones$X-C_6H_4-CH=CHCOCH_3$	0.505 (6)	

* In the present work.
** Calculated from the data of Blomfield and Fuchs (1), taking $\rho_{benz} = 2.431$ (3).

It follows from Table 2 that the relative $\rho_{\text{trans}} = 0.539$ obtained by us for the dissociation of cinnamic acids agrees well with the values of ρ_{trans} for ester hydrolysis and for the reaction of isotopic hydrogen exchange, whereas $\rho_{\text{cis}} = 0.422$ is appreciably smaller than the relative ρ_{trans}.

The result obtained in the present work, namely that in trans-cinnamic acids the influence of substituents is transmitted more effectively than in cis-cinnamic acids, can be understood by considering the mechanism of transmission of the effect in these systems.

Three principal mechanisms are known for the transmission of substituent effects through a double bond conjugated with a benzene ring: 1) the inductive effect; 2) the conjugation effect; 3) the field effect.

It may be assumed that the transmission of substituent effects by the induction mechanism is the same in the cis and trans isomers, while the field effect is greater in the case of the cis isomer. As for the conjugation effect, it is apparently greater in the trans isomer, as follows from the data on the UV spectra of substituted cis- and trans-cinnamic acids [2] and their esters [1]. In trans-cinnamic acids and esters, a shift of the absorption maximum into the long-wavelength region and higher extinction coefficients are observed, which indicates greater conjugation in these systems.

From consideration of Stuart-Briegleb models for cis- and trans-cinnamic acids, it is evident that in cis acids, because of steric hindrance, coplanarity is disturbed (by up to 35–40°) between the plane of the benzene ring and the double bond, which is evidently the reason for the decrease in conjugation in cis-cinnamic acids. Thus, the more effective transmission of substituent effects in the series of trans-cinnamic acids, as compared with the cis isomers, is apparently due to greater conjugation in these acids.

Thus, in the present work a comparative quantitative evaluation of the transmission of substituent effects in the series of cis- and trans-cinnamic acids has been carried out, and it has been shown that in the series of trans-cinnamic acids the transmission of substituent effects occurs more effectively than in the series of cis-cinnamic acids.

Experimental Part

Substituted trans-cinnamic acids were synthesized from the corresponding substituted benzaldehydes by the Doebner reaction [8,9].

$$X{-}C_6H_4CHO + CH_2(COOH)_2 \rightarrow X{-}C_6H_4{-}CH{=}CHCOOH + H_2O + CO_2.$$

Unsubstituted cis-cinnamic acid was obtained by selective hydrogenation of the ethyl ester of phenylpropiolic acid over a Lindlar catalyst ($Pd/CaCO_3$) [8], followed by alkaline hydrolysis of the ester.

Substituted cis-cinnamic acids were obtained by UV irradiation of the trans isomers [10,11]. For this purpose the trans acid was dissolved either in an ammonia solution, as in the case of *m*-nitrocinnamic acid, or in a soda solution and irradiated for 20–30 days with a PRK-4 UV lamp. Fractional precipitation of the cis and trans acids was then carried out from the resulting solution of their salts; in this process the trans acid precipitated first. From the last fractions, after several recrystallizations, the pure cis acid was obtained. The cis acid was also isolated by extraction with ether of the solution obtained after precipitation of the acids. Yields of cis acids were from 20 to 45%. cis-*p*-Bromocinnamic acid was obtained for the first time.

Found, %: C 47.53; H 3.16; Br 34.75
Calculated, %: C 47.60; H 3.08; Br 35.21

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Note: Figure translations are in progress. See original paper for figures.