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Abstract

Full Text

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On the Transmission of the Influence of Substituents by Various Conjugated Systems

In a previous paper (¹) we showed that the Hammett equation is applicable to the reaction of isotopic hydrogen exchange. This conclusion was drawn as a result of studying the influence of substituents on the rate of isotopic exchange of the hydrogen of the methyl group in *p*-substituted acetophenones (I).

$$\mathrm{X}-\langle\ \ \rangle-\mathrm{COCH_3} \tag{I}$$

As is known, the Hammett equation establishes a quantitative relationship between the reactivity of compounds of the benzene series and the nature of the substituent in the para or meta positions,

$$\lg\frac{k}{k_0}=\sigma\rho,$$

where k is the rate constant of the reaction (equilibrium) of the substituted compound, k_0 is the rate constant of the reaction (equilibrium) of the unsubstituted compound, σ is the substituent constant, which depends only on the nature of the substituent and its position in the benzene ring, and ρ is the reaction constant.

According to Jaffé (²), the reaction constant ρ depends on three factors: 1) the efficiency with which the electronic influence of the substituent is transmitted to the reaction center; 2) the sensitivity of the reaction to a change in electron density at the reaction center; 3) the reaction conditions.

Thus, by comparing the values of ρ for one and the same reaction under identical conditions for molecules possessing different systems of conjugated bonds, one can quantitatively evaluate the efficiency of transmission of the substituent influence through these systems.

In the present work, the influence of substituents on the rate of the hydrogen-exchange reaction of para-substituted benzalacetophenone (trans) (II) and para-substituted 4′-acetyldiphenyls (III) was studied

$$X - \langle\ \rangle - CH{=}CH - COCH_3, \tag{II}$$

$$X - \langle\ \rangle - \langle\ \rangle - COCH_3. \tag{III}$$

For this purpose, the rate constants of the hydrogen-exchange reaction at 20°, calculated according to a first-order equation, were determined for benzalacetophenone, *p*-dimethylaminobenzalacetophenone, *p*-methoxybenzalacetophenone, *p*-nitrobenzalacetophenone, *p*-chlorobenzalacetophenone, *p*-bromobenzalacetophenone (see Table 1), and for 4′-acetyldiphenyl, 4-nitro-4′-acetyldiphenyl, 4-bromo-4′-acetyldiphenyl, 4-methoxy-4′-acetyldiphenyl, and 4-chloro-4′-acetyldiphenyl (see Table 1). The conditions of the hydrogen-exchange reaction were the same as in the case of para-substituted acetophenones. The reaction was carried out in absolute ethyl alcohol containing deuterium in the hydroxyl group, with sodium ethoxide as catalyst.

Table 1

Ketone	X (substituent)	k_{20°, sec^{-1}	σ-para*
$X{-}C_6H_4{-}CH{=}CHCOCH_3$	H	$(5.15 \pm 0.49) \cdot 10^{-5}$	0
$X{-}C_6H_4{-}CH{=}CHCOCH_3$	NO_2	$(1.76 \pm 0.20) \cdot 10^{-4}$	0.788
$X{-}C_6H_4{-}CH{=}CHCOCH_3$	$(CH_3)_2N$	$(1.01 \pm 0.14) \cdot 10^{-5}$	−0.83
$X{-}C_6H_4{-}CH{=}CHCOCH_3$	CH_3O	$(2.48 \pm 0.26) \cdot 10^{-5}$	−0.268
$X{-}C_6H_4{-}CH{=}CHCOCH_3$	Br	$(9.72 \pm 1.50) \cdot 10^{-5}$	0.232
$X{-}C_6H_4{-}CH{=}CHCOCH_3$	Cl	$(9.70 \pm 1.50) \cdot 10^{-5}$	0.227
$X{-}C_6H_4{-}C_6H_4{-}COCH_3$	H	$(3.65 \pm 0.55) \cdot 10^{-5}$	0
$X{-}C_6H_4{-}C_6H_4{-}COCH_3$	NO_2	$(9.42 \pm 1.20) \cdot 10^{-5}$**	0.778
$X{-}C_6H_4{-}C_6H_4{-}COCH_3$	CH_3O	$(3.60 \pm 0.52) \cdot 10^{-5}$	−0.262
$X{-}C_6H_4{-}C_6H_4{-}COCH_3$	Br	$(6.42 \pm 0.53) \cdot 10^{-5}$	0.232
$X{-}C_6H_4{-}C_6H_4{-}COCH_3$	Cl	$(6.40 \pm 0.50) \cdot 10^{-5}$	0.227

* The σ-para values are taken from the table of McDaniel and Brown (^{4}).

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

** Earlier (^{1}) the value $k_{20^\circ} = 6.69 \cdot 10^{-5}$ sec^{-5} was given; in the present work it has been refined.

The dependence of the logarithm of the rate constant of the hydrogen-exchange reaction of para-substituted benzalacetone (Fig. 1) and para-substituted 4′-acetyldiphenyl (Fig. 2) on the substituent constants σ-para is linear. Thus, it was shown that the Hammett equation is obeyed also

Fig. 1

Fig. 2

for the hydrogen-exchange reaction of para-substituted benzalacetone and para-substituted 4′-acetyldiphenyl, just as for para-substituted acetophenones. For all the systems we investigated, values of the constant ρ were calculated; they proved to be: for the acetophenone system (I), 1.6; for the benzalacetone system (II), 0.8; for the 4′-acetyldiphenyl system (III), 0.4.

In the ketones under consideration, the substituent is separated from the reaction center by different systems of conjugated bonds, namely by a benzene ring, a double bond conjugated with a benzene ring, and the diphenyl system.

Comparing the values of ρ for these ketones with one another, one can, as indicated above, quantitatively evaluate the effectiveness of transmission of substituent effects through a benzene ring, a double bond conjugated with a benzene ring, and the diphenyl system.

Taking the value of ρ for the acetophenone system as unity, we obtain the relative values of ρ: for the acetophenone system (I), 1; for the benzalacetone system (II), 0.50; for the 4′-acetyldiphenyl system (III), 0.25.

The data obtained are in good agreement with the results reported in the work of Berliner and Liu (^{3}), where relative values of ρ were calculated for the hydrolysis (in 88.7% ethanol) of ethyl esters of substi-

substituted benzoic acids ($\rho_{\text{rel}} = 1$), cinnamic acids ($\rho_{\text{rel}} = 0.53$), and diphenylcarbonic acids ($\rho_{\text{rel}} = 0.24$). However, the same authors give relative values of ρ for the dissociation of the corresponding acids: benzoic acids ($\rho_{\text{rel}} = 1$), cinnamic acids ($\rho_{\text{rel}} = 0.47$), diphenylcarbonic acids ($\rho_{\text{rel}} = 0.37$), and these values differ somewhat both from the relative ρ values for ester hydrolysis and from the data obtained by us for the hydrogen isotope-exchange reaction.

Thus, from a comparison of the relative ρ values obtained by us for the hydrogen isotope-exchange reaction of para-substituted acetophenone, benzalacetone, and 4′-acetyldiphenyl, and considering the steric factors of these molecules in this reaction to be the same, one may, following Berliner (^{3}), conclude that in the hydrogen-exchange reaction a double bond conjugated with a benzene ring transmits only 0.50 of the electronic effect of the substituent, while the diphenyl system transmits only 0.25 of this effect in comparison with a single benzene ring.

Experimental Part

The hydrogen-exchange reaction of the ketones studied was carried out in abs. deuteroethanol (with a deuterium content in the hydroxyl of 8–10 at. %), with sodium ethoxide as catalyst (as a solution in deuteroethanol). The concentration of sodium ethoxide in the reaction solution was 0.00036 N. Deuteroethanol was taken in large excess: 1 mole of ketone per 200–800 moles of deuteroethanol, depending on the solubility of the ketone. Special experiments showed that, under the conditions we selected, the rate of the hydrogen-exchange reaction does not depend on a two- to fourfold change in the amount of deuteroethanol.

The hydrogen-exchange reaction was stopped by cooling to −80°, whereupon the ketones precipitated. Only in the case of benzalacetone and *p*-chlorobenzalacetone, in order to stop the reaction, was the reaction mixture poured into water (the volume of water being 25 times the volume of the sample).

The deuterium content was determined by the drop method (^{5}). The authors consider it their duty to express gratitude to Prof. A. I. Shatenshtein, Ya. M. Varshavsky, E. A. Yakovleva, and O. P. Gei for their great assistance in mastering this method.

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