

A SIMPLE EXPLANATION FROM THE SIGN OF ρ- VALUE FOR THE KIND OF CHARGE THAT DEVELOPS IN THE INTERMEDIATE OR THE TRANSITION STATE OF A REACTION SERIES: A ONE-HOUR PHYSICAL-ORGANIC CHEMISTRY GRADUATE CLASSROOM LECTURE

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Abstract. The sign of ρ (Hammett's reaction constant) in the ionization of benzoic acids is unit positive; therefore it follows that any reaction series with positive ρ value will have the same center of charge in magnitude on the transition state. And if the sign of ρ turns out to be negative for some reaction series it implies that reaction site in the transition state will have positive sign. This is one of the vital, fundamental conclusions of Hammett's linear free energy relation (LFER). An outsized number of reaction series religiously conform to this fundamental conclusion. In this article, we have strived to explicate this fundamental conclusion to graduate and undergraduate students by taking the illustration of several reactions with different Hammett reaction constants. In Scheme 5 the students can examine simultaneous negative and positive Hammett's ρ values in a solitary reaction. Thus it is expedient for a professor to give Scheme 5 reaction series to exemplify the relation between sign of rho and the charge on the transition state in his lecture on Hammett's equation.

Keywords: Hammett's reaction constant, transition state, intermediate.

Introduction

Hammett (1935, 1937) first formulated the structure-reactivity correlations. If we browse the literature we can find several reaction series on the application of

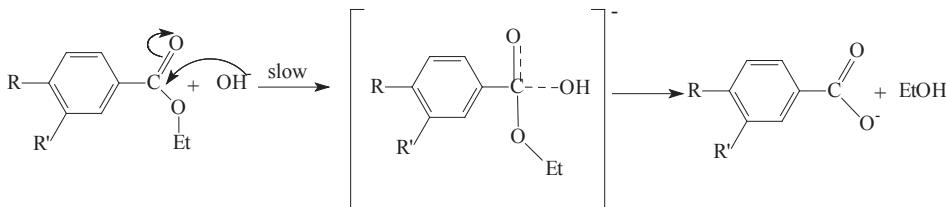
Hammett's relation. We have illustrated the title axiom with some putative reactions (Jaffe, 1953). To witness a prominent substituent effect, the essential requisite for any reaction is, either, a complete positive or a complete negative charge should develop or disappear, in the intermediate or the transition state involved in the rate determining step, during the course of the reaction relative to the reactant or the product respectively.

Results and discussion

Reactions with strong and moderately strong positive Hammett's ρ values

With the realization that substituent constants can be determined with the aid of Hammett's equation, it is now possible to obtain reaction constants for a wide catalog of organic reactions. The archetypal reaction is the alkaline hydrolysis of ethyl benzoate ($R = R' = H$) in water/ethanol mixture at 30°C. Measurement of the reaction rate k_0 , combined with that of many substituted ethyl benzoates (Scheme 1) eventually results in a Hammett reaction constant of +2.5 (Hammett, 1937; Evans et al., 1937). In fact this value is taken as Taft's ρ^* value in formulating the σ^* values for aliphatic and α -substituted benzene derivatives.

Scheme 1



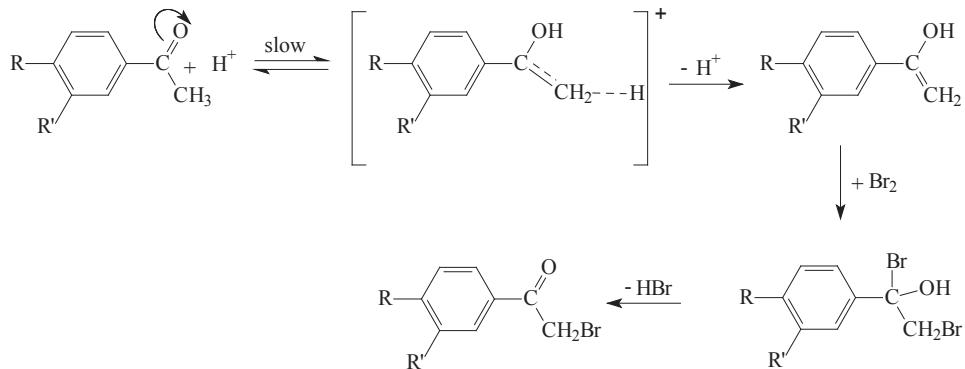
It is understandable from the above mechanism (Scheme 1) that this base-catalyzed reaction illustrates a noteworthy response to substituent polar effects because reactant proceeds from a neutral species to a completely negatively charged intermediate in the rate- determining (slow) step. The neutral species acquires a complete negative charge. This reaction is of the kind in which a neutral species proceeds towards a negatively charged species. Hence a Hammett reaction constant of + 2.5 is justified. Here the readers may conceive that the Hammett's ρ value would be unity, but it is + 2.5. The magnitude of the ρ value depends on several factors like the stability of the transition state. The

two other well acknowledged examples of this kind of reactions are: The ionization of phenols having a Hammett ρ value of 2.00 (Judson & Kilpatrick, 1949) and the base catalyzed hydrolysis of cinnamic acid esters having a Hammett ρ value of 1.3 (Kindler, 1927; Jaffe, 1953). Here we would like to drive home the fact that Hammett ρ value of 1.3 is almost half of the Hammett's reaction constant of base catalyzed hydrolysis of benzoate esters (+2.5). This is explained in terms of attenuation effect (Jagannadham, 2009), where in if the reaction site moves away from the substituent by increasing the chain length between the benzene ring and the reaction site, the magnitude of the Hammett's ρ decreases.

Reactions with slight positive and zero Hammett's ρ values

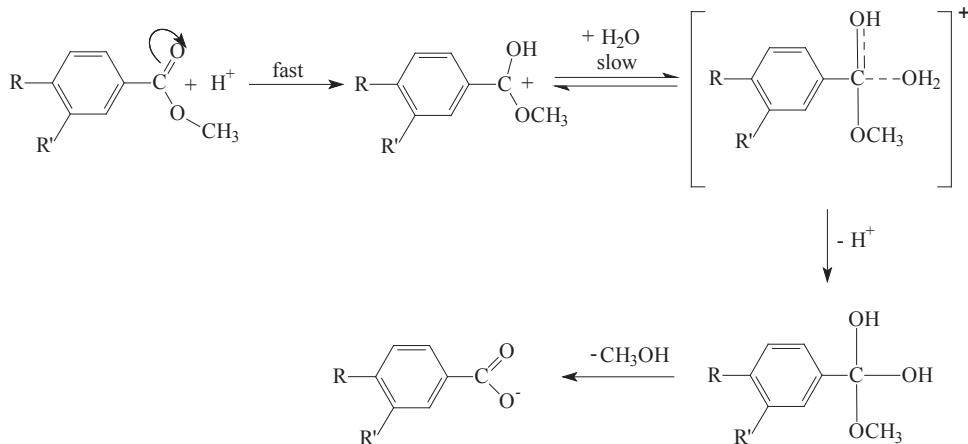
Acid catalyzed bromination of substituted acetophenones (Scheme 2) in an acetic acid/water/hydrochloric acid mixture gave a Hammett's ρ value of + 0.42 (Nathan & Watson, 1933; Morgan & Watson, 1935; Jaffe, 1953).

Scheme 2



In Scheme 2 again a neutral species becomes a positively charged species in the rate determining step, hence a negative Hammett's ρ value is expected but instead a small positive Hammett's ρ (+ 0.42) was observed. The acid catalyzed de-esterification (Timm & Hinshelwood, 1938; Jaffe, 1953) of substituted benzoic esters (scheme 3) in ethanol gave a negligibly small negative Hammett's ρ value (-0.085).

Scheme 3

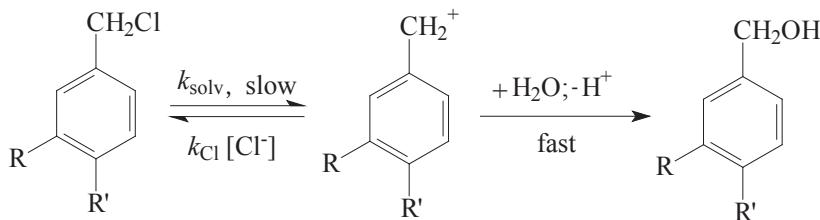


In the above (Scheme 3) rate-determining step, a positively charged species is advancing towards a positively charged species. Here the net change in charge is zero. Hence a negligible substituent effect (Hammett's ρ value of - 0.085) is observed.

Reactions with strong negative Hammett's ρ value

Solvolytic solvolysis of substituted benzyl chlorides (Olivier, 1922; Jaffe, 1953) - Scheme 4 in acetone-water at 69.8°C gave a Hammett's ρ of - 1.88.

Scheme 4



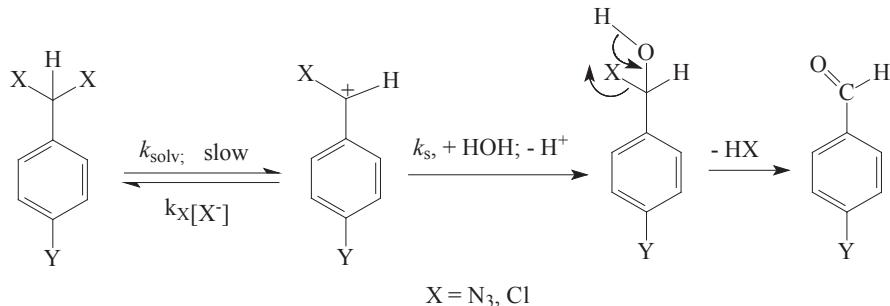
In the rate-determining step of the above solvolysis, neutral reactant is advancing towards a completely positive species, hence Hammett's ρ value - 1.88 is substantiated.

Observation of simultaneous negative and positive Hammett's ρ values in a single reaction

An appreciable amount of work was done by one of the authors (VJ) elsewhere (Richard et al., 1995) and from our laboratory (Sanjeev & Jagannadham, 2002) in this

direction, on the solvolysis of benzyl-*gem*-diazides and benzyl-*gem*-dichlorides in aqueous solution. The conceivable mechanism suggested, for the solvolysis of these reactions is depicted in Scheme 5.

Scheme 5



Solvolytic step (k_{solv}) of above scheme involves development of complete positive charge from a neutral species and hence strong negative ρ (Hammett's) values of - 3.8 (for $X = N_3$) (Richard et al., 1995) and - 2.05 (for $X = Cl$) (Sanjeev & Jagannadham, 2002). The addition of water (k_s) to the cation suffers a loss of complete positive charge which indirectly is intelligible in terms of gain of complete negative charge. Hence moderate positive ρ values (Hammett's) of + 1.6 (for $X = N_3$) and + 1.18 (for $X = Cl$) are observed for this step.

Conclusions

The reaction constant, or sensitivity constant, ρ , describes the susceptibility of the reaction to substituent effect relative to the ionization of benzoic acids. It is equivalent to the slope of the Hammett plot. Information on the reaction, including that related to mechanism can be obtained based on the value of ρ . If the value of: (1) $\rho > 1$, the reaction is more sensitive to substituents than that to benzoic acid and negative charge develops during the reaction (or positive charge is lost); (2) $0 < \rho < 1$, the reaction is less sensitive to substituents than that to benzoic acid and again negative charge develops (or positive charge is lost); (3) $\rho = 0$, no sensitivity to substituents, and no charge is built or lost; (4) $\rho < 0$, the reaction builds positive charge (or loses negative charge)

These relations can be exploited to elucidate the mechanism of a reaction. As the value of ρ is related to the charge developed or disappeared during the rate determining step, mechanisms can be formulated based on this information. If the mechanism for the reaction of an aromatic compound is thought to occur through one of the two mechanisms, the compound can be modified with substituents with different σ values

and kinetic measurements made. Once these measurements have been made, a Hammett plot can be constructed to determine the value of ρ . If one of these mechanisms involves the formation of charge, this can be verified based on the ρ value. Conversely, if the Hammett plot shows that no charge is developed, i.e. a zero slope, the mechanism involving the building of charge can be rejected.

Thus this simple protocol explicates the kind of charge the transition state of a reaction series develops from the sign of ρ value.

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