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Light Induced Hydrolysis of Substituted Phenylacetates

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ABSTRACT

The substituent effect on light induced hydrolysis of phenyl acetates was studied by irradiating these acetates and calculating the percentage of hydrolysis product from the integration ratio of acetate methyl and aromatic protons after getting ^{1}H NMR of photolysis mixture.

Keywords: Light induced hydrolysis, Phenylacetate, Substituent effect, Acetonitrile.

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INTRODUCTION

In order to study the substituent effect on light induced hydrolysis of phenylacetates, by having various subtituents in the aromatic ring, the work incorporated in this paper was undertaken. Substituted phenylacetate were prepared from the acetic anhydride and the corresponding phenol and then subjected to photolysis. The residue was subjected to NMR spectroscopy and calculations based on the integration of aliphatic and aromatic region suggested that hydrolysis has taken place upto the extent of 18.5% in the case of phenylacetate(II) whereas p-cresyl acetate(IV) showed hydrolysis upto the extent of 16%.

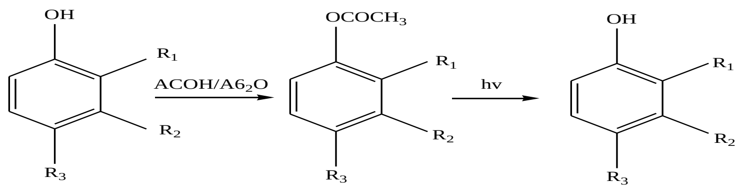
However, when p-bromophenylacetate (VI) was subjected to photolysis in aqueous acetonitrile for the same period under similar conditions, the percentage of hydrolysis calculated from integration of aliphatic and aromatic region suggested that the hydrolysis took place upto the extent of 20.8%. p-Nitrophenylacetate (VIII) under similar conditions gave the hydrolysis products to the tune of 30.5% as calculated on basis of integration curves of NMR spectrum of the residue obtained after evaporation of the solvent and acetic acid from the reaction mixture. m-Nitrophenylacetate (X), on the other hand, on being irradiated in aqueous acetonitrile (1:5) for 15hr. underwent hydrolysis upto the extent of 25.7% but surprisingly enough the o-nitrophenylacetate (XII) when irradiated in aqueous acetonitrile (1:5) for 15hr under identical conditions gave the hydrolysis product only in 3% quantity as determined on the basis of NMR spectroscopy. The extra-ordinary low yield could probably be due to steric hindrance near the site of reaction.

In order to further establish the theory of steric hindrance as mentioned above, α-naphthylacetate (XIV) was irradiated in aqueous acetonitrile (1:5) for 15hr and the NMR spectroscopy of the resultant mixture obtained from the photolysate suggested that the hydrolysis has taken place only up to the extent of 3.1% thereby confirming that steric hindrance is responsible for low percentage of hydrolysis in o-nitrophenylacetate (XII). In order to distinguish whether the low percentage in α-naphthylacetate (XIV) was due to steric hindrance or nature of naphthalene ring, β-naphthylacetate (XVI) was irradiated in aqueous acetonitrile under identical conditions and the hydrolysis took place upto extent of 21.1% as calculated from the integration curves of NMR spectrum of reaction mixture. This further confirmed the theory of steric hindrance. The various percentage obtained in these experiments is summarized in table - 1. [1-5]

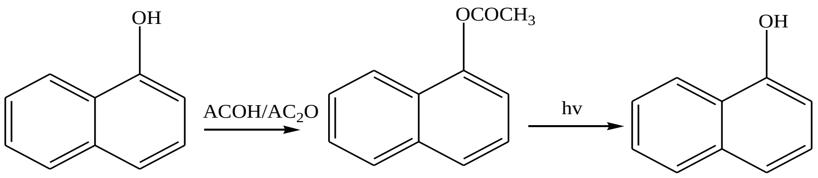
Table -1

p-Nitrophenyl acetate	30.5%
m-Nitrophenyl acetate	25.7%
o-Nitrophenylacetate	3.0%
p-Bromophenylacetate	20.8%
Phenylacetate	18.5%
p-Cresylacetate	16.0%
β-Naphthylacetate	21.1%
α-Naphthylacetate	3.0%

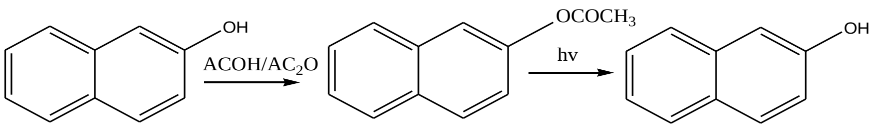
The rationale for the varying percentage of hydrolysis could be offered by consideration of the fact that the electron withdrawing groups will create electron deficiency on the carbon atom to which phenolic oxygen is attached which in turn will withdraw electron from the carbonyl carbon and ester oxygen bond thereby increasing the electron deficiency on the carbonyl carbon. On the other hand the electron releasing groups will increase electronic density on the ring carbon attached to the oxygen atom which in turn will increase the electronic density (decrease electron deficiency). Consequently, the rate of hydrolysis will be higher in the cases where the carbonyl carbon is having electron deficiency or in other words +ve charge in comparison to one where +ve charge is less. This trend is very well exhibited by various substituents (Cf table-1), except the o-substituents wherein the steric factors near the reaction centre increase steric hindrance thereby drastically decreasing the rate of hydrolysis. Same trend is observed in hydrolysis of α-naphthylacetate in comparison to β-naphthylacetate.



I : $R_1=R_2=R_3=H$	II : $R_1=R_2=R_3=H$	I : $R_1=R_2=R_3=H$
II : $R_1=R_2=H$, $R_3=CH_3$	IV : $R_1=R_2=H$, $R_3=CH_3$	III : $R_1=R_2=H$, $R_3=CH_3$
V : $R_1=R_2=H$, $R_3=Br$	VI : $R_1=R_2=H$, $H_3=Br$	V : $R_1=R_2=H$, $R_3=Br$
VII : $R_1=R_2=H$, $R_3=NO_2$	III : $R_1=R_2=H$, $R_3=NO_2$	VII : $R_1=R_2=H$, $R_3=NO_2$
IX : $R_1=R_3=H$, $R_2=NO_2$	XI : $R_1=R_3=H$, $R_2=NO_2$	IX : $R_1=R_3=H$, $R_2=NO_2$
XI : $R_2=R_3=H$, $R_1=NO_2$	XII : $R_2=R_3=H$, $R_1=NO_2$	XI : $R_2=R_3=H$, $R_1=NO_2$



(XIII) (XIV) (XIII)



(XV) (XVI) (XV)

DISCUSSION

A series of esters including benzoic esters containing substituent were examined by Taft [1,2]. The reactivity of many ortho substitueted esters towards hydrolysis is most certainly affected by steric factors arising from the close proximity of bulky groups to the reaction centre [3-5]. The relation of the parent benzoic esters to other esters is given σ* relative to formate as σ* as 0.11. The σ* values for the ortho-substituted benzoic esters relative to benzoic ester are set out in the table and are believed to be purely polar values, and hence one would like to compare them with meta or para- σ values, which are also purely polar for a different reason. In the benzene ring, one has complication of interior conjugation and so Taft makes comparison primarily with para- σ values in the belief that the conjugative contributions to the conveyance of polarity from the substituent to the test group are more nearly comparable as between o- and p-, than between o- and m-substituents.

Suppose steric effects have been completely eliminated, one still do not expect the two sets of constants to be identical, for, first, the field effect will be differently weighted in the two positions: and second, the polar paths, though analogously composed of conjugation and induction are by no means identical. But one should expect purely polar substituent constants to follow similar trends in the two positions.

Taft proposed that the changes induced by substituents in log k or log K in reactions other than those of ester hydrolysis (for which substituent constants σ* can be determined) will be found proportional to the σ* values of the substituents as given by ester hydrolysis. This proposition may be written,

$$\log (K/Ko) \text{ or } \log (k/Ko) = \rho^* \sigma^*$$

where p* is an empirically determined proportionality constant for the reaction. In graphical terms, this means that log k or log K, plotted against σ*, should give a straight line of slope ρ. The plot of σ vs log K/Ko gives a straight line and the value of calculated ρ is found to be 0.25.

Table – 2

	Me_2N	**MeO**	**F**	**Cl**	**Me**	**CN**	**NO_2**
	-	0.11	0.34	0.37	-0.07	0.56	0.71
σ m σ^+	-	0.05	0.33	0.40	-0.07	0.56	0.67
	-0.83	-0.27	0.06	0.23	-0.17	0.66	0.78
	-1.7	-0.78	-0.07	0.11	-0.31	0.65	0.79
σ p σ^+ σ^-	-	-	-	-	-	1.00	1.27

EXPERIMENTAL

Melting points were determined in open capillary tubes and are uncorrected. ^1H NMR spectra on Bruker Avance II 400 MHz NMR spectrometer using tetramethylsilane as internal standard and chemical shift values are reported in δ scale.

GENERAL PROCEDURE

Substituted phenylacetate (1×10^{-3}M) were irradiated in aqueous acetonitrile (1:5) in a pyrex photoractor for a period of 15hr. The photolysate was diluted with water and the reaction product taken up in chloroform and evaporation of the solvent gave a mixture of substituted phenol (CVI), acetic acid and unreated substituted phenylacetate from which acetic acid was removed under reduced pressure. The residue, thus obtained, was dissolved in a deuterated solvent and its NMR spectrum was recorded. The percentage of hydrolysis product was calculated from the integration ratio of acetate methyl and the aromatic protons.

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