SHORT COMMUNICATIONS

STERIC EFFECT OF ALKYL GROUPS

S. SUGUNAN
Department of Applied Chemistry, University of Cochin, Cochin 682 022, India.

THE idea that alkyl groups release electrons inductively when attached to electron-withdrawing substituents has secured wide acceptance[1-4]. Recently, however, Charton has provided evidence for the view that the effect of alkyl groups in certain types of ester hydrolysis is essentially steric[5]. We have sought to study the problem in another way. The thermodynamic pK_a values of the esters of acid *tere*phthalic and acid phthalic esters have been determined in seven solvent systems. The effect on acidity in the first series of the alkyl groups can only be of polar origin (inductive and hyperconjugative) while in the second series the steric effect may also be involved. The steric effect can be expected to affect the acidity by interfering with the intramolecular hydrogen bonding between the carboxyl and ester groups. The data are set out in table 1. The values were determined potentiometrically[6], with potassium chloride as the ionic medium. The salt concentration range was 0.01-0.10 *M*. The ester concentrations were in the range 10^{-3} to 10^{-4} *M*.

The significant features are:(i) the values for the acid *tere*phthalic esters are essentially independent of the nature of the alkyl group in any one solvent. (ii) the values increase with the size of the alkyl group in the acid phthalic esters. The first result can be understood only on the basis that the alkyl group is not releasing electrons by the inductive mechanism. The second is rationalised by assuming that with an increase in the size of the alkyl group, there is greater interference with intramolecular hydrogen bonding with consequent decrease in acidity. We believe the results to be significant in that, the study involves only equilibria and so do not involve any assumption regarding the nature and structure of the transition state or the relative importance of steric and polar effects in determining the free-energy of activation. However, it does not necessarily follow that alkyl groups do not show an inductive effect under all circumstances.

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TABLE 1

Thermodynamic pk_a values of acid terephthalic and phthalic esters in various solvent systems at 32° C

Ester	Solvent						
	DMSO (%, v/v) in water				Ethanol (%, v/v) in water		
	70	50	20	Water	20	50	70
Ethyl hydrogen *tere*phthalate	7.77	6.10	4.25	3.66	4.04	5.73	6.48
n-Propyl hydrogen *tere*phthalate	7.77	6.07	4.30	3.61	4.06	5.69	6.45
iso Propyl hydrogen *tere*phthalate	7.70	6.08	4.28	3.61	4.06	5.68	6.40
iso Butyl hydrgoen *tere*phthalate	7.69	6.11	4.26	3.63	4.02	5.73	6.40
t-Butyl hydrogen *tere*phthalate	7.73	6.12	4.29	3.60	4.04	5.75	6.46
Methyl hydrogen phthalate	7.63	5.79	3.89	3.05	3.63	5.06	5.75
iso Propyl hydrogen phthalate	8.23	6.13	4.14	3.26	4.08	5.50	6.16
t-Butyl hydrogen phthalate	8.29	6.27	4.46	3.42	4.17	5.69	6.24
t-Amyl hydrogen phthalate	8.24	6.34	4.52	3.41	4.21	5.77	6.23

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BROMINATION OF BENZENE AND SUBSTITUTED BENZENES WITH POTASSIUM BROMATE.—A KINETIC STUDY

L. PUTTARJUNAN AND N. VENKATASUBRAMANIAN
Department of Chemistry, RKM Vivekananda College, Madras 600 004, *India*.

ALTHOUGH potassium bromate in sulphuric acid is to known[1] to brominate benzene into bromobenzene, potassium bromate has hardly ever been used as a brominating agent for aromatics. It is only in the last two years that some interest has been shown on the synthetic utility in reactions[1,2]. Yet, no kinetic work is on record to determine the mechanism of this reaction. We report in this communication, the preliminary results of such an investigation.

Benzene and other aromatics (both deactivated as well as activated) undergo facile bromination in aqueous acetic acid in the presence of added sulphuric acid. These are conditions under which very little reaction takes place with molecular bromine. The amount of sulphuric acid needed obviously varies with the system—deactivated aromatics requiring a much larger percentage of the mineral acid. The reactions follow a simple rate-law. For the bromination of benzene.

$$\frac{-d\,[\mathrm{Br}(V)]}{dt} = k_2\,(\text{benzene})\quad [\mathrm{Br}(V)]$$

No simple correlation could be established between rate and acidity. Due to the electrophilic nature of the reagent, the highest rates are obtained with activated aromatics such as toluene or *p*-xylene. Tables 1 and 2 summarize some of the data for these experiments. The rates were followed by an iodometric assay of the unracted bromate (V) at suitable time intervals under pseudo first-order conditions.

TABLE 2

Substrate	$10^5 k_1 \mathrm{sec}^{-1}$
Benzene*	4.64
Toluene*	39.17
p-cxylene*	90.3
Acetanilide*	333
Benzoic acid§	34.4
Nitrobenzene§	2.69
Chlorobenzene§	256
Benzene§	938
[Substrate]=0.05M	Temp: 50° C
$[BrO^-_3]$=0.005M	Solvent: 50% HOAC-50% H_2O

*1.0M H_2SO_4
§3.0M H_2SO_4.

As the deactivated aromatics lead to a single product (*viz.* the meta-nitroderivative), the data for benzoic acid and nitrobenzene in table 2 (with that for benezene, statistically corrected for the six nuclear positions) was subjected to a Hammett analysis using the Brown-Okamoto σ values. The Hammett rho of −3.1, though on the low side, underscores the electrophilic nature of the substitution process.

TABLE

[Benzene] M	$[BrO^-_3]$ M	$10^5.k_1 \mathrm{sec}^{-1}$ $[H_2SO_4]$	$10^4 k_2$ lit.mol.$^{-1}$ sec^{-1}	
0.05	0.004	1	4.62	9.20
0.05	0.005	1	4.64	9.28
0.05	0.007	1	4.58	9.16
0.07	0.005	1	6.58	9.40
0.10	0.005	1	9.56	9.56
0.05	0.005	2	343	
0.05	0.005	3	938	
Temp: 50° C		Solvent: 50% HOAc 50% H_2O		