Notes

Kinetics of Esterification of *ortho-*Substituted Phenoxyacetic, Phenylmercaptoacetic, Phenylsulphinylacetic & Phenylsulphonylacetic Acids with Diazodiphenylmethane in Dimethylformamide

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Rate constants for the esterification of *ortho-*substituted phenoxyacetic, phenylmercaptoacetic, phenylsulphinylacetic and phenylsulphonylacetic acids with diazodiphenylmethane in dimethylformamide at 30°, 40° and 50°C have been determined. The results obey the Hammett equation well, revealing that the steric effect of substituents does not operate herein.

In a previous paper[1] we reported the kinetics of esterification of *meta-* and *para-*substituted phenoxyacetic, phenylmercaptoacetic and phenylsulphonylacetic acids with diazodiphenylmethane. In this note we report the results of spectrophotometric study of the kinetics of esterification of the title acids where COOH is separated by OCH_2(phenoxyacetic acid), SCH_2(phenylmercaptoacetic acid) $SOCH_2$(phenylsulphinylacetic acid) or SO_2CH_2 (phenylsulphonylacetic acid) with diazodiphenylmethane in dimethylform amide at 30°, 40° and 50°C.

All the substrates and diazodiphenylmethane were prepared in the laboratory as per literature methods and their purity checked.

Diazodiphenylmethane reacts with carboxylic acids as follows:

$$RCOOH + Ph_2CN_2 \rightarrow RCOOCHPh_2 + N_2$$
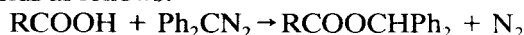
In aprotic solvents diazodiphenylmethane reacts with carboxylic acids by a step-wise mechanism with the rate limiting proton transfer from the carboxylic acid to form the diphenylmethyldiazonium carboxylate ion pair as the first step[2]. In dimethylformamide, the acid may be assumed to be almost monomeric and that the course of the reaction will be analogous to that in alcohols[3] but without ether formation. Therefore the rate constants measured in this solvent are second order rate constants corresponding to the reaction between diazodiphenylmethane and monomeric carboxylic acids.

The results reported in Table 1 indicate that electron-withdrawing groups increase the rate

Table 1 — Rate Constants for Esterification of *ortho-*Substituted Phenoxyacetic, Phenylmercaptoacetic, Phenylsulphinylacetic and Phenylsulphonylacetic Acids with Diazodiphenylmethane in Dimethylformamide

Substituent	k (dm³ mol⁻¹ min⁻¹) at					
	30°	40°	50°C	30°	40°	50°C
	Phenoxyacetic acid			Phenylmercaptoacetic acid		
H	0.24	0.48	0.95	0.16	0.35	0.69
Cl	0.33	0.57	1.39	0.26	0.50	1.15
Br	0.32	0.57	1.35	0.26	0.49	0.98
CH_3	0.22	0.38	0.74	0.16	0.34	0.70
OCH_3	0.18	0.32	0.62	0.14	0.29	0.56
NO_2	0.56	1.06	2.02	0.48	0.97	1.87
	Phenylsulphinylacetic acid			Phenylsulphonylacetic acid		
H	0.80	1.51	2.99	0.91	2.12	4.79
Cl	1.04	1.72	3.16	1.47	3.00	5.68
Br	1.05	1.74	3.30	1.51	3.13	5.85
CH_3	0.66	1.15	2.20	0.95	1.92	4.17
OCH_3	0.56	0.98	1.88	0.67	1.42	3.30
NO_2	1.94	3.56	6.36	2.40	5.09	8.73

Table 2 — Rate Constants for the Esterification of *para-* and *meta-* Substituted Phenylsulphinylacetic Acids with Diazodiphenylmethane in Dimethylformamide

Substituent	k (dm³ mol⁻¹ min⁻¹) at			Substituent	k (dm³ mol⁻¹ min⁻¹) at		
	30°	40°	50°C		30°	40°	50°C
p-F	0.85	1.59	3.16	*p*-OCH_3	0.60	1.15	2.29
p-Cl	1.04	1.91	3.76	*p*-NO_2	1.78	3.35	6.46
p-Br	1.05	1.88	3.80	*m*-CH_3	0.74	1.40	2.74
p-CH_3	0.67	1.25	2.51	*m*-Cl	1.19	2.24	4.32

Table 3 — ρ_o/ρ_p Values for Four Series of Acids at 30°C

Bridging group	ρ_o	ρ_p	(ρ_o/ρ_p)
-OCH_2-	0.457	0.456	0.983
-SCH_2-	0.546	0.595	0.918
-$SOCH_2$-	0.526	0.455	1.156
-SO_2CH_2-	0.576	0.440	1.309

while reverse is the case with electron-donating groups. The order of reactivities of these acids is: phenylsulphonylacetic acids > phenylsulphinylacetic acids > phenoxyacetic acids > phenylmercaptoacetic acids.

In the reactions of *meta-* and *para-*substituted phenoxyacetic, phenylmercaptoacetic and phenylsulphonylacetic acids with diazodiphenylmethane (DDM) in dimethylformamide[1], the Hammett equation was obeyed with high precision. The results on the kinetics of the reaction of *meta-* and

para substituted phenylsulphinylacetic acids presented in Table 2 also obey very well the Hammett equation.

A comparison of the ρ_o values obtained (employing σ_p values) for the *ortho*-substituted reaction series with the ρ_p *values obtained for the para*-substituted reaction series shows that ρ_o/ρ_p ratio is close to unity for different side chains as given in Table 3. This may mean that the *ortho*-substituents transmit the electrical effect almost to the same extent in these series of reactions as the *para* substituents.

References

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2 Mose O'Ferral R A, Kwok W K & Miller S I, *J Am chem Soc*, **86** (1964) 5553.
3 Roberts J D & Watanabe W J, *J Am chem Soc*, **72** (1950) 4869.