AROMATIC SULPHONATION VIII*

Partial rate factors in the sulphonation of toluene with aqueous sulphuric acid

BY

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The ratio of the overall rate constants for the sulphonation of toluene and benzene in aqueous sulphuric acid at 25° decreases from 110 to 25 on varying the acid concentration from 78 to 92 wt-%. Similar trends are observed at 5° and 45°.

The partial rate factors for *ortho-*, *meta-* and *para*-substitution in the sulphonation of toluene with aqueous sulphuric acid all decrease strongly with increasing acid concentration. The partial rate factor for *para*-substitution is temperature independent, indicating a negligible difference in activation enthalpy between substitution at the *para*-position in toluene and at a single position in benzene. The corresponding difference in activation entropies is 7 ± 2 cal · deg^{-1} · mole^{-1}.

The latter difference is ascribed to differences in solvation of the starting hydrocarbons or/and of the transition states. These differences in solvation may also be responsible for the small but apparent deviations from the Selectivity Relationship observed in the present study. It is suggested that the sulphonation of toluene and benzene in aqueous sulphuric acid proceeds via a Wheland type of intermediate.

Introduction

Electrophilic aromatic substitution reactions, like nitration and halogenation, have been studied extensively in the last twenty years and partial rate factors for these types of substitution reactions have been obtained for a large number of compounds [1, 2].

The chemical literature is still lacking partial rate factors for aromatic sulphonation. We therefore thought it of interest to determine such partial rate factors. Toluene was regarded as an attractive compound to start with. Accordingly we set out to determine the rate of sulphonation of toluene

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[1] P. B. D. de la Mare and J. H. Ridd, "Aromatic substitution: Nitration and Halogenation", Academic Press, New York, 1959.
[2] A. V. Topshiev, "Nitration of Hydrocarbons and other Organic Compounds", Pergamon Press, 1959.

and benzene, as well as the isomer distribution in the sulphonation of toluene under similar experimental conditions.

In a preliminary communication we have reported the partial rate factors for the homogeneous sulphonation of toluene in 82.9 wt-% aqueous sulphuric acid at 25.0° as $f_p{}^{Me}$ 258, $f_m{}^{Me}$ 5.7 and $f_o{}^{Me}$ 63.4 [3]. Recently *Eaborn* and *Taylor* [4] have reported partial rate factors for the sulphonation of toluene in aqueous sulphuric acid [4]. However these data should be considered tentatively as the relative rate data [4, 5] and the isomer distribution data, employed in their calculation, were determined under different reaction conditions.

Results and discussion

Rate constant ratios for the homogeneous sulphonation of toluene and benzene in aqueous sulphuric acid, $_tk_{exp}/_{be}k_{xp}$, — calculated from the pre-

Table I

Sulphonation of toluene in aqueous sulphuric acid

Temp. °C	H_2SO_4, wt-%	$\dfrac{_tk_{exp}}{_{b}k_{exp}}$	$f_p{}^{Me}$	$f_m{}^{Me}$	$f_o{}^{Me}$	S_f	b
5.0 ± 0.5	81.9 ± 0.2	106	418	7.6	100	1.74	1.51
	87.2	35.6	112	3.2	47.2	1.54	1.33
	91.0	15.7	43.6	1.9	23.2	1.36	1.21
	93.4	12.5	33.3	1.7	19.1	1.29	1.18
	95.9	9.5	24.9	1.34	14.7	1.27	1.10
25.0 ± 0.5	77.8 ± 0.2	106 [a]	491	6.7	69	1.86	1.45
	78.2	101	458	7.0	67	1.82	1.46
	80.0	113	487	8.0	86	1.78	1.51
	82.9	68	267	7.4	85	1.56	1.55
	84.3	47.1	174	4.1	51	1.63	1.37
	86.2	41.1	140	3.7	49.6	1.58	1.36
	87.3	25.1	82	2.5	32.1	1.52	1.26
	91.0	29.8	86	3.4	41.7	1.40	1.38
45.0 ± 0.5	77.6 ± 0.2	92	430	12.0	51	1.55	1.69
	81.9	69	288	8.5	54	1.53	1.61
	84.0	53	206	6.5	49.3	1.50	1.54
	87.2	37.4	129	4.9	43.1	1.42	1.49
	89.1	29.3	94	4.4	36.3	1.33	1.48

[a] *A. J. Prinsen*, private communication.

[3] *H. Cerfontain, A. W. Kaandorp* and *F. L. J. Sixma*, Rec. trav. chim. **79**, 935 (1960).
[4] *C. Eaborn* and *R. Taylor*, J. Chem. Soc. **1960**, 1480.
[5] *V. Gold* and *D. P. N. Satchell, ibid.* **1956**, 1635.
[6] *A. F. Holleman* and *P. Caland*, Ber. **44**, 2504 (1911).

viously reported pseudo first order rate constants for benzene [7] and toluene [8] — are collected in Table I. The data show that the rate constant ratio decreases rapidly with increasing acid concentration (*cf.* Fig. 1). This large
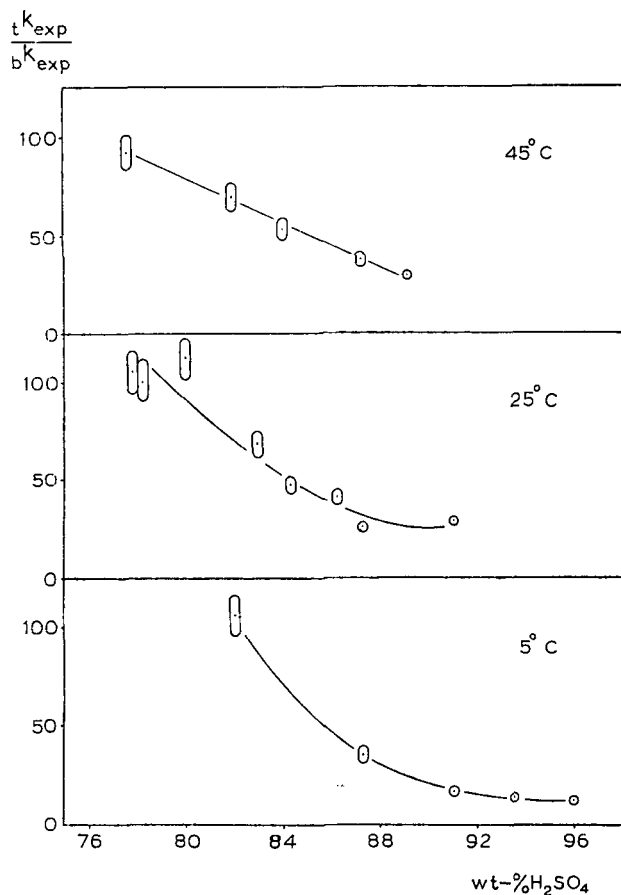

Fig. 1.   Variation of the overall rate constant ratio for the sulphonation of toluene and benzene with sulphuric acid concentration.

variation in $_tk_{exp}/_bk_{exp}$ is in contrast to the constant value of 31 $\pm$ 1.5 at 25.0° reported by *Eaborn* and *Taylor* for the acid range of 77.4-81.4 wt-% sulphuric acid [4]. This latter value seems questionable to us, as it was calculated from rate data for benzene [5] which deserve consideration [7].

[7] *A. W. Kaandorp, H. Cerfontain* and *F. L. J. Sixma,* Rec. trav. chim. **81,** 969 (1962).
[8] *Idem, ibid.* **82,** 113 (1963).

Partial rate factors

The partial rate factors for the sulphonation of toluene were calculated from the $_t k_{exp}/_b k_{exp}$ ratio (cf. Table I), combined with figures for the isomer distribution, obtained previously in our laboratory [9]. The results are collected in Table I. For all acid concentrations $f_p{}^{Me} > f_o{}^{Me} \gg f_m{}^{Me}$. As shown in Fig. 2, $\log f_p{}^{Me}$ decreases rapidly with increasing acid concentration. The points of $\log f_p{}^{Me}$ for 5°, 25° and 45° seem to fall on the
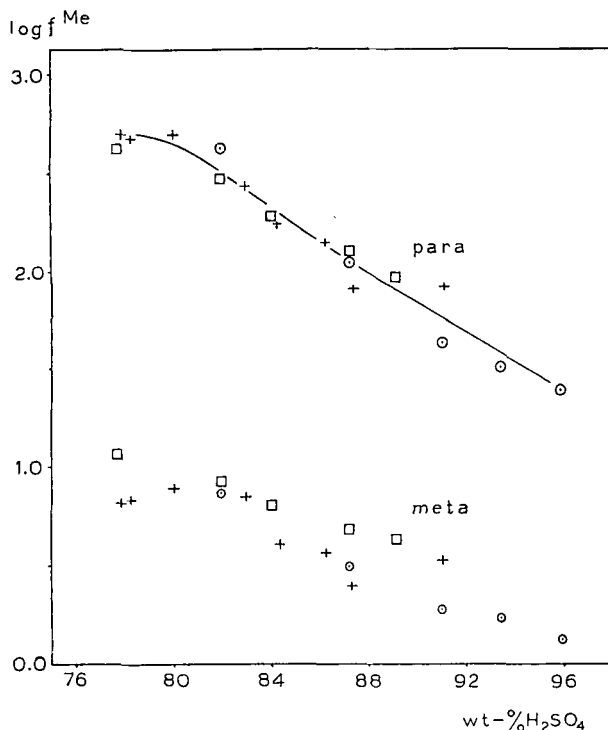

Fig. 2. Partial rate factors for *para*- and *meta*-substitution in the sulphonation of toluene; dependence on sulphuric acid concentration (⊙ 5.0°; + 25.0°; □ 45.0°).

same line, indicating that for a given acid concentration $f_p{}^{Me}$ is independent of temperature. The decrease in $\log f_m{}^{Me}$ with increasing sulphuric acid concentration is smaller than that of $\log f_p{}^{Me}$; this has been taken as an indication of increasing reactivity of the sulphonation entity with increasing acid concentration [9]. The points for $\log f_m{}^{Me}$ at the three temperatures studied seem to scatter at random. The decrease in the $f_p{}^{Me}/f_o{}^{Me}$ ratio with increasing acid concentration has been attributed to a decrease in

[9] *H. Cerfontain, F. L. J. Sixma* and *L. Vollbracht, Rec. trav. chim.* **82,** 659 (1963).

steric hindrance for *ortho*-substitution due to a decrease in the solvation of the *ortho*-transition state with increasing acid concentration [9].

Activation parameters

The constancy of log f_p [Me] with variation in temperature calls for some further discussion. Accordingly, the differences in activation parameters were calculated for three sulphuric acid concentrations in accordance with: [10a]

$$f_p{}^{Me} = \exp\left[(\Delta S_{p-t}{}^{\ddagger} - \Delta S_b{}^{\ddagger}) / R\right] \cdot \exp\left[- (\Delta H_{p-t}{}^{\ddagger} - \Delta H_b{}^{\ddagger}) / RT\right] \qquad [1]$$

in which $\Delta S^{\ddagger}$ is the activation entropy, $\Delta H^{\ddagger}$ the activation enthalpy and the indices p-t and b refer to *para*-substitution in toluene and to substitution of a single position in benzene. The activation enthalpy difference increases from -1.7 ± 0.7 to -0.3 ± 0.7 kcal·mole^{-1} on varying the sulphuric acid con-

Table II

Differences between activation parameters for sulphonation of the *para*-position in toluene and a single position in benzene [a].

H$_2$SO$_4$, wt-%	$f_p{}^{Me}$			$\Delta H_{pt}{}^{\ddagger} - \Delta H_b{}^{\ddagger}$ kcal · mole^{-1}	$\Delta S_{pt}{}^{\ddagger} - \Delta S_b{}^{\ddagger}$ cal · deg^{-1} · mole^{-1}
	5.0°	25.0°	45.0°		
81.9 ± 0.2	418	301	288	−1.7 ± 0.7	5.9 ± 2.2
85.5	185	150	153	−0.8 ± 0.5	7.2 ± 1.9
89.1	101	85	94	−0.3 ± 0.7	7.9 ± 2.3

[a] The activation parameters and their standard deviations were determined by least square calculations [11] in acordance with [1].

centration from 81.9 to 89.1 wt-% (*cf.* Table II). The differences seem small in view of the positive inductive and polarisability effects of the methyl group, especially at the higher acid concentrations. The difference in activation entropy of about 7 ± 2 cal·deg^{-1}·mole^{-1} (*cf.* Table II) is unexpected also*. Both these deviations from the commonly expected behaviour for electrophilic substitution may originate in solvent effects, *viz.* differences in solva-

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* A similar observation is reported for the dedeuteration of *p*-D-toluene and D$_1$-benzene in solutions of sulphuric acid in trifluoroacetic acid, in which case $\Delta S_{p-t}{}^{\ddagger} - \Delta S_b{}^{\ddagger} = 10$ cal · deg^{-1} · mole^{-1} [12].

[10] *S. Glasstone, K. J. Laidler* and *H. Eyring*, "The Theory of Rate Processes", McGraw-Hill Book Co., Inc. New York, 1941, a: p. 198, b: p. 404, c: p. 402.

[11] *W. J. Youden*, "Statistical Methods for Chemists", John Wiley and Sons, Inc. New York, 1951, p. 41-43.

[12] *E. L. Mackor, P. J. Smit* and *J. H. van der Waals*, Trans. Faraday Soc. **53**, 1309 (1957).

tion *. A separation of these solvent effects is brought about in equation [2]: [10b]

$$f_{\text{p}}^{\text{Me}} = (f_\text{t} \cdot f_\text{b}^\ddagger / f_\text{b} \cdot f_{\text{p}-\text{t}}^\ddagger) \cdot \exp\left[(\Delta S'_{\text{p}-\text{t}}^\ddagger - \Delta S'_\text{b}^\ddagger) / R\right] \cdot \exp\left[(\Delta H'_{\text{p}-\text{t}}^\ddagger - \Delta H'_\text{b}^\ddagger) / RT\right] \quad [2]$$

in which f_b, f_t, $f_\text{b}^\ddagger$ and $f_{\text{p}-\text{t}}^\ddagger$ are the activity coefficients of benzene, toluene, the transition state for substitution in benzene and the transition state for *para*-substitution in toluene, respectively and in which the dotted activation parameters refer to "internal" activation parameters [10c].

The activity coefficient ratio f_b/f_t equals 1.14 in 80.6 wt-% sulphuric acid at 25° [13]. At present nothing seems to be known about the temperature variation of this activity coefficient ratio. The ratio $f_\text{b}^\ddagger/f_{\text{p}-\text{t}}^\ddagger$ will be very difficult to determine; however, one may assume this ratio to vary in a similar way to f_b/f_t. In due course we propose to undertake a study of the solubility of aromatic hydrocarbons in aqueous sulphuric acid in order to obtain information on the temperature dependence of the activity coefficients. At present no evidence can be furnished to support our suggestion that solvent effects are responisble for the anomalies in the activation parameter differences.

A discussion on the differences between the activation parameters for sulphonation at the *ortho-*, *meta-* and *para*-position in toluene has been given previously [9].

Test of the Selectivity Relationship

It has been suggested by *Brown* that electrophilic aromatic substitution reactions are governed by a linear free energy relationship: [14]

$$\log f_\text{p} = b \cdot \log (f_\text{p}/f_\text{m}) \qquad [3]$$
$$\log (f_\text{p}/f_\text{m}) = S_t \qquad [4]$$

in which S_t was termed the selectivity factor. Relationship [3] was shown to be derivable from the *Hammett* equation [15], with

$$b = \sigma_\text{p}/(\sigma_\text{p} - \sigma_\text{m}) \qquad [5]$$

in which σ_p and σ_m are the substituent constants for *para-* and *meta*-substitution, respectively. Attempts to correlate electrophilic aromatic substitution with Hammett's side chain substituent constants were found to be unsuccessful for those substituents which could exhibit resonance

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* The activation energy for monosulphonation of benzene in aqueous sulphuric acid decreases rapidly with increasing acid concentration [7]. This variation is likely to originate in solvent effects as well.

[13] S. Olsson, Arkiv Kemi 15, 259 (1960).
[14] H. C. Brown and L. M. Stock, J. Am. Chem. Soc. 84, 3298 (1962).
[15] C. W. McGary, Y. Okamoto and H. C. Brown, ibid. 77, 3037 (1955).

interaction with the reaction centre in the transition state [16-18]. Accordingly, *Brown* proposed a new series of substituent constants, σ^+, for application to electrophilic aromatic substitution. Three methods were suggested to determine these σ^+ substituent constants, *viz.* from solvolysis rate constants of t-cumyl chlorides, from the selectivity relationship [3] and by an "extended selectivity treatment" [14]. For the methyl group, the calculated values for *b* by these methods are 1.23, 1.33 and 1.30, respectively.

For the sulphonation of toluene in aqueous sulphuric acid the selectivity factor S_f decreases with increasing acid concentration (*cf.* Table I). Values of *b*, calculated according to [3], are listed in Table I. The data show that *b* decreases from 1.6 to about 1.1 by varying the sulphuric acid concentration from 78 to 96 wt-% sulphuric acid (*cf.* Fig. 3) The observed deviations from the constant value of 1.3, as determined for *b* by *Brown* [14], probably originate in solvation differences of the transition state and/or of the aromatic hydrocarbons*.
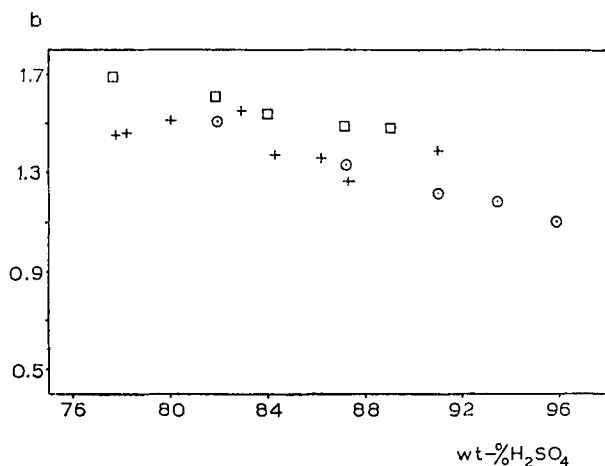

Fig. 3.   Dependence of *b* on sulphuric acid concentration ($\odot$ 5.0°; + 25.0°; $\square$ 45.0°).

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* The *Hammett* side chain relationship applies to reactions in which the entropy is variable only in those cases, where the activation enthalpy is a linear function of the entropy [19]. It seems likely that similar restrictions apply to the Selectivity Relationship.

[16] *J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain* and *R. Zagt,* J. Am. Chem. Soc. **76**, 4525 (1954).

[17] *P. B. D. de la Mare,* J. Chem. Soc. **1954,** 4450.

[18] *J. R. Knowles, R. O. C. Norman* and *G. K. Radda, ibid.* **1960,** 4885.

[19] *J. E. Leffler,* J. Org. Chem. **20,** 1202 (1955); *P. R. Wells,* Chem. Revs. **63,** 171 (1963).

[20] *G. A. Olah, St. J. Kuhn* and *S. H. Flood,* J. Am. Chem. Soc. **83,** 4571 (1961).

Large deviations from the selectivity relationship have been observed in aromatic nitration with nitronium tetrafluoroborate in tetramethylene-sulphone as solvent [20], which were ascribed to the π-complex character of the transition state. The deviations observed in the present study are thought to be of minor character only. Consequently, it is suggested that the sulphonation of simple aromatic hydrocarbons in aqueous sulphuric acid proceeds via a Wheland type of intermediate (or σ-complex).

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