

297. *Aromatic Reactivity. Part IX.\* Sulphonation of Toluene by Water-Sulphuric Acid and by Trifluoroacetic Acid-Water-Sulphuric Acid.*

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Using isotopic dilution analysis, we have measured the rate of sulphonation of toluene in 75–84 wt.-% sulphuric acid and in trifluoroacetic acid containing aqueous sulphuric acid. In the aqueous medium, sulphonation of toluene shows the same dependence on the concentration of acid as does that of benzene, but is  $31 \pm 1.5$  times as fast. This ratio, combined with available figures for the isomeric composition of the product, corresponds with partial rate factors of 34, 4.2, and 112, respectively, for *ortho*-, *meta*-, and *para*-positions of toluene.

IN connexion with studies of acid-catalysed aromatic detritiation we have measured the rate of sulphonation of toluene in homogeneous solution in 75.3–84.1 wt.-% aqueous sulphuric acid at 25.0°. To do this we measured the rate of disappearance of  $\alpha$ -tritiated toluene by extracting the toluenesulphonic acids with aqueous alkali and determining the activity of the residual toluene.† (Hydrogen exchange at the  $\alpha$ -position is negligible under the reaction conditions; cf. ref. 1.)

[H <sub>2</sub> SO <sub>4</sub> ] (wt.-%) .....	75.30	77.67	79.80	81.14	84.14
10 <sup>6</sup> k (sec. <sup>-1</sup> ) .....	1.76	8.68	35.9	97.6	923

The first-order rate constants,  $k$ , are shown in the Table. The variation of the rate of sulphonation with the sulphuric acid concentration is the same as that<sup>2</sup> for benzene. A plot of  $\log k$  against the wt.-% of sulphuric acid is an excellent straight line,‡ parallel to that for benzene, and from the plots it is found that toluene reacts  $31 \pm 1.5$  times as fast as benzene at any particular acid concentration in the range studied. This factor (the uncertainty in which arises from the scatter of the points in the plot for benzene§) is considerably larger than that (5.1) which was observed for sulphonation in nitrobenzene at 40°<sup>3</sup> and, in absence of any direct measure, was previously assumed to apply approximately to reactions in aqueous sulphuric acid.<sup>4,5</sup>

Holleman and Caland<sup>6</sup> measured the isomer distribution for sulphonation of toluene in 96 and 100 wt.-% sulphuric acid (but with a sulphuric acid : toluene ratio of 4.4, much lower than we used) at several temperatures, and figures for 25° may be obtained by interpolation. Since the proportion of *meta*-product is somewhat different for 96 and 100% acid (*viz.*, 4.5 and 5.5%) it would be desirable to have the isomer distribution measured for 84% acid, the strongest we used. But the properties of sulphuric acid change more in the 100–96% region than in 96–84% region, and furthermore the  $\log k$ -[H<sub>2</sub>SO<sub>4</sub>] plots for benzene and toluene show no sign of departing from parallelism, so that the factor of 31.5 could reasonably be assumed to apply at somewhat higher acid concentrations than those studied. Thus the uncertainty in applying the isomer distributions in 96% acid to rate

\* Part VIII, *J.*, 1960, 179.

† In principle a small difference in reactivity between toluene and [ $\alpha$ -<sup>3</sup>H]toluene might exist, but it is most unlikely that this would exceed our experimental error.

‡ A plot of  $\log k$  against the  $H_0$  acidity function (Paul and Long, *Chem. Rev.*, 1957, 57, 1) is also an excellent straight line, with a slope of -2.3, but it is unlikely that this has any fundamental significance.

§ If allowance is made for the possible error of  $\pm 20\%$  in each of the rates for benzene,<sup>2</sup> the uncertainty is  $\pm 7$ , but the errors may largely cancel in the  $\log k$ -[H<sub>2</sub>SO<sub>4</sub>] plot.

<sup>1</sup> Ollson and Melander, *Acta Chem. Scand.*, 1954, 8, 523.

<sup>2</sup> Gold and Satchell, *J.*, 1956, 1635.

<sup>3</sup> Stubbs, Williams, and Hinshelwood, *J.*, 1948, 1065.

<sup>4</sup> Gold and Satchell, *J.*, 1956, 2743.

<sup>5</sup> Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, 75, 6292.

<sup>6</sup> Holleman and Caland, *Ber.*, 1911, 44, 2504.

measurements in 75–84% acid is probably no larger than that inherent in the original determinations of the isomer proportions. Using isomer distributions for 96% acid at 25° obtained from Holleman and Caland's data (*viz.*: *ortho*, 36; *meta*, 4.5; *para*, 59%), we arrive at the following partial rate factors:  $f_o^{\text{Me}}$ , 34;  $f_m^{\text{Me}}$ , 4.2;  $f_p^{\text{Me}}$ , 112. The figures for the *ortho*- and the *para*-position are probably fairly accurate, but that for the *meta*-position may be distinctly less so.

For a large number of electrophilic aromatic substitutions for which accurate results are available, Stock and Brown<sup>7</sup> have recently shown that the ratio  $(\log f_p^{\text{Me}})/(\log f_m^{\text{Me}})$  has values of 3.18 to 4.72. Our figures lead to a value of 3.3 for this ratio, and thus (in marked contrast to the figures calculated<sup>5</sup> by using the toluene : benzene rate-ratio for sulphonation in nitrobenzene) are in reasonable agreement with generalizations advanced by Brown and his co-workers.<sup>5,7</sup>

We have also measured the rate of sulphonation of toluene in trifluoroacetic acid containing aqueous sulphuric acid. The results are as follows (the figures in parentheses denoting mole-percentages):

Medium ...	CF <sub>3</sub> ·CO <sub>2</sub> H(82.36)–H <sub>2</sub> SO <sub>4</sub> (14.47)–H <sub>2</sub> O(3.17)	CF <sub>3</sub> ·CO <sub>2</sub> H(93.60)–H <sub>2</sub> SO <sub>4</sub> (2.45)–H <sub>2</sub> O(3.95)
10% (sec. <sup>-1</sup> )	955	2.58
Medium ...	CF <sub>3</sub> ·CO <sub>2</sub> H(85.94)–H <sub>2</sub> SO <sub>4</sub> (7.84)–H <sub>2</sub> O(6.22)	
10% (sec. <sup>-1</sup> )	18.8	

For a given concentration of sulphuric acid, sulphonation is much faster in such media than in aqueous acid. Semiquantitative experiments, not here described, indicated that for a fixed concentration of sulphuric acid in trifluoroacetic acid the rate of sulphonation falls very sharply as water is added up to a few moles-%.

#### EXPERIMENTAL

[ $\alpha$ -<sup>3</sup>H]Toluene.—Tritiated water (2 ml.), of 50 mc/ml. activity, was added to the Grignard reagent from benzyl bromide (19 g.) and magnesium (2.8 g.) in ether (80 ml.). Excess of water was then added and the ether layer was separated, washed, dried (Na<sub>2</sub>SO<sub>4</sub>), and fractionally distilled to give [ $\alpha$ -<sup>3</sup>H]toluene (6.7 g.), b. p. 110°,  $n_D^{20}$  1.4947.

Rate Measurements.—[ $\alpha$ -<sup>3</sup>H]Toluene (*ca.* 0.05 ml.) was shaken for 10 min. with sulphuric acid (*ca.* 260 ml.) of known strength in a stoppered 1 l. flask. Five 50 ml. portions were transferred by automatic pipette into tubes of 51–53 ml. capacity. (A drainage time of 1½ min. was allowed, this having been found to give accurately reproducible quantities.) The tubes were sealed with Teflon-sleeved stoppers and placed in a bath at 25.0° (kept constant within ±0.02°). The first tube was withdrawn after 20–30 min. and the others at known times, *t*. The contents of each tube were transferred, with washing, to a 250 ml. flask containing toluene (10 ml.) and ice-water (*ca.* 130 ml.), and the flask was sealed with a Teflon-sleeved stopper and shaken mechanically for 15 min. The toluene layer was separated, and washed successively with water, 10% aqueous sodium hydroxide, and water, and then dried (Na<sub>2</sub>SO<sub>4</sub>). Any yellow colour was removed with activated charcoal. The relative activities of the extracts were measured by using weighed amounts in a simple liquid-scintillation method in which a galvanometer deflection proportional to the activity is measured.<sup>8</sup> (Full details of the method will be given in a future paper of this series.) Two activity measurements were made on each extract. Rate constants were calculated from the formula  $kt = 2.303 \log [D_0/(D_0 - D_t)]$  where  $D_0$  and  $D_t$  are the deflections (for 4 g. of the toluene extract) at times  $t = 0$  and  $t = t$ ; they did not vary from the mean by more than ±2% for 80% or more of reaction. Mean rate constants, normally determined graphically, could be duplicated within 2%. The following represents a typical run:

<i>t</i> (sec.) .....	0	21,600	86,400	115,200	169,200
<i>D</i> (mm.) .....	44.2	36.7	21.0	16.4	10.4
10% <i>k</i> (sec. <sup>-1</sup> ) .....	—	8.64	8.62	8.61	8.55

For reactions in trifluoroacetic acid–water–sulphuric acid, *ca.* 0.05 ml. of [ $\alpha$ -<sup>3</sup>H]toluene was dissolved in *ca.* 5.5 ml. of the medium; 1 ml. portions were pipetted into drawn-off glass tubes

<sup>7</sup> Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3323.

<sup>8</sup> Matsukawa and Eaborn, *Research*, 1956, **9**, S 37; Eaborn, Matsukawa, and Taylor, *Rev. Sci. Instr.*, 1957, **28**, 725.

which were then sealed and placed in the thermostat, the solutions being kept ice-cold throughout the mixing, dividing, and sealing. On removal, each tube was broken under a mixture of 2% aqueous sodium hydroxide (100 ml.) and toluene (10 ml.) in a flask which was then sealed with a Teflon-sleeved stopper and shaken for 15 min. The toluene layer was separated, washed with water, and dried, and its activity was determined as before. Because a significant amount of the sulphuric acid is used up and a significant amount of water is formed in these media, the first-order rate constants fall off as reaction proceeds (the more so the higher the  $\text{CH}_3 \cdot \text{C}_6\text{H}_5 : \text{H}_2\text{SO}_4$  ratio), and the constants given are those obtained by extrapolation to zero time. They are believed to be accurate to within  $\pm 5\%$ .

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