Aromatic Sulphonation. Part 75.[1] Intramolecular Kinetic Isotope Effects of Hydrogen in the Aprotic Sulphonation of 1,2,4,5-Tetramethylbenzene, Naphthalene, and 1,6-Methano[10]annulene. Implications for the Mechanism of the Sulphur Trioxide Sulphonation

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The intramolecular substrate kinetic isotope effects of hydrogen for the sulphonation of 1,2,4,5-tetramethyl[3-^{2}H]-benzene and [1,4-$^2H_2$]naphthalene with sulphur trioxide in nitromethane as solvent at 0 °C have been determined as k_H/k_D = 5.6 ± 0.6 and 1.8 ± 0.1, respectively. With trichlorofluoromethane as solvent at −25 °C the intramolecular isotope effects for these two substrates are 3.1 ± 0.3 and 2.0 ± 0.1 respectively. For the sulphonation of 1,6-methano[2,7-$^2H_2$][10]annulene in dioxan at 12 °C k_H/k_D = 3.8 ± 0.3. The observed primary kinetic isotope effects are discussed in terms of the previously established σ,σ-mechanism for aromatic sulphonation with sulphur trioxide in aprotic solvents. They are ascribed to steric hindrance accompanying the intramolecular proton shift of the 1-arenium-1-pyrosulphonate σ-complex, yielding the arenepyrosulphonic acid. For trichlorofluoromethane as solvent the occurrence of an ' encounter complex ' is discussed.

AROMATIC sulphonation has been the object of various mechanistic studies, especially the sulphonation with aqueous and fuming sulphuric acid which has been extensively reviewed.[2] Recently we also reported on the mechanism of aromatic sulphonation with chlorosulphuric acid.[3]

A good decade ago we initiated a study to elucidate the mechanism of the aprotic aromatic sulphonation with sulphur trioxide.[4] The sulphonation with sulphur trioxide in CCl_3F as solvent is very fast,[4b,5] and even the use of a complexing solvent like nitromethane [6] did not moderate the sulphur trioxide reactivity sufficiently to allow the rate determination of non-deactivated aromatic substrates, such as benzene,† by classical means.[4b,5] Based on the mechanistic studies with *p*-dichlorobenzene using both CCl_3F and $MeNO_2$ as a solvent, and with chlorobenzene using $MeNO_2$ as a solvent, it was proposed that the sulphonation proceeds by reactions (1)—(3).

$$ArH + SO_3 \underset{-1}{\overset{1}{\rightleftharpoons}} \overset{+}{Ar}\begin{matrix}SO_3^-\\H\end{matrix} \quad (1)$$

$$\overset{+}{Ar}\begin{matrix}SO_3^-\\H\end{matrix} + SO_3 \underset{-2}{\overset{2}{\rightleftharpoons}} \overset{+}{Ar}\begin{matrix}S_2O_6^-\\H\end{matrix} \quad (2)$$

$$\overset{+}{Ar}\begin{matrix}S_2O_6^-\\H\end{matrix} \xrightarrow{3} ArS_2O_6H \quad (3)$$

In view of the second-order rate dependence on sulphur trioxide, the consumption of two equivalents of sulphur trioxide, and the absence of a kinetic isotope effect of hydrogen for the sulphonation in nitromethane as solvent,[4b] the rate-limiting step for that solvent was taken to be (2). The sulphonation in dioxan as solvent probably proceeds similarly.‡ In the non-complexing solvent CCl_3F the sulphonation rate is first order in sulphur trioxide, but its consumption again two equivalents.[4a] The rate-limiting step for that solvent was therefore proposed to be (1). The absence of a difference in the rate of sulphonation of [$^1H_4$]- and [$^2H_4$]-*p*-dichlorobenzene in CCl_3F as solvent [4a] is in agreement with the rate-limiting character of step (1). The object of the present study was to obtain more information on the mechanism of aprotic sulphonation, especially for non-complexing solvents.

The sulphonation of [1,3,5-$^2H_3$]benzene [5] and [2-^{2}H]-1,3,5-trimethylbenzene [9] in both CCl_3F and $MeNO_2$ proceeds without a primary kinetic isotope effect for hydrogen. The 9-substitution of anthracene with sulphur trioxide in dioxan as solvent gives k_H/k_D = 7 ± 1.[10] This maximal primary kinetic isotope effect was explained in terms of a strong retardation of the proton removal from the σ-complex due to steric hindrance between the incoming sulphonate group and the two *peri*-hydrogens. Anthracene-9-sulphonic acid (in contrast to *e.g.* benzenesulphonic acid) is a very labile sulphonic acid which already desulphonates in the presence of water or dilute mineral acid.[11]

The effect of the steric requirement at the reaction centre on the size of the kinetic isotope effect in electrophilic aromatic substitution [12] is further apparent from (i) the occurrence of a substantial primary kinetic isotope effect in the nitration of 2,4,6-tri-t-butylnitrobenzene [13] and anthracene,[14] and (ii) the bromination of a series of polyalkylbenzenes (k_H/k_D increases in the order benzene < pentamethylbenzene < 5-t-butyl-1,2,3-trimethylbenzene < 1,3,5-t-butylbenzene).[15] The steric requirements for electrophilic aromatic substitution increase in the order nitration < bromination < sulphonation.[16] Accordingly it was of interest to learn whether the steric hindrance for sulphonation of 1,2,4,5-tetramethylbenzene would give rise to a primary kinetic isotope effect. Further, also in relation to our recent interest in 10π electron aromatic systems,[17] we have determined the kinetic isotope effects of naphthalene and

† The determination of the rate of sulphonation of benzene with sulphur trioxide was attempted in a flow system by Rattcliff.[7]

‡ An attempt was made to elucidate the mechanism of the sulphur trioxide sulphonation in dioxan as solvent.[8] The reaction was found to suffer from decomposition of the solvent leading to a complicated sulphonation rate equation for high substrate converion. However, the zero-time extrapolated rate equation is similar to that for nitromethane as (complexing) solvent, *viz.* $v = k[ArH][SO_3]^2$.

TABLE 1

Substrate kinetic isotope effect of hydrogen in electrophilic substitution of aromatic hydrocarbons

Type of substitution	Substrate	Isotopic composition substrate (%) $^2H_0 : {}^2H_1 : {}^2H_2 : {}^2H_3$	Reagent	Solvent	Temp. (°C)	k_H/k_D	Isotopic composition unconcerted substrate (%) $^2H_0 : {}^2H_1 : {}^2H_2 : {}^2H_3$	Ref.
Sulphonation	1,2,4,5-Tetramethyl-[3-^{2}H]benzene	11.8 : 88.2 : 0.0	SO_3	$MeNO_2$	0	5.6 ± 0.6	12.8 : 87.0 : 0.2	
				CCl_3F	−25	3.1 ± 0.3	22.2 : 72.0 : 5.7	
	[1,4-$^2H_2$]Naphthalene	1.2 : 97.3 : 1.5	SO_3	$MeNO_2$	0	1.8 ± 0.1	: 3.3 : 90.4 : 6.3	
				$MeNO_2$	25	1.8 ± 0.1		
				CCl_3F	−25	2.0 ± 0.1	0.3 : 97.4 : 2.3	
	1,6-Methano-[2,7-$^2H_2$][10]-annulene	0.9 : 8.9 : 90.2 : 0.0	SO_3	Dioxan	12	3.8 ± 0.3		
	[1,3,5-$^2H_3$]Benzene		SO_3	$MeNO_2$	20	1.3 ± 0.1		5
				CCl_3F	−35	1.2 ± 0.1		
	1,3,5-Trimethyl-[2-^{2}H]benzene		SO_3	$MeNO_2$	0	1.1[5] ± 0.1[3]		8
				CCl_3F	−35	0.98 ± 0.09		
	[9-^{2}H]Anthracene		SO_3	Dioxan	40	6.8 ± 1.2		10
Nitration	[1,4-$^2H_2$]Naphthalene		NO_2BF_4	Sulpholan	30	1.15 ± 0.05		14
				MeCN	1	1.08 ± 0.05		
	[9-^{2}H]Anthracene		NO_2BF_4	Sulpholan	30	2.6 ± 0.3		14
				MeCN	1	6.1 ± 0.6		
Bromination	1,3,5-Trimethyl-[2,4,6-$^2H_3$]-benzene + 1,3,5-trimethylbenzene		Br_2	AcOH	30	1.10 ± 0.02		15
	Pentamethyl[6-^{2}H]-benzene + pentamethylbenzene		Br_2	AcOH	18	1.20 ± 0.05		15

1,6-methano[10]annulene. It was reported that the sulphonation of naphthalene with sulphur trioxide in dichloroethane proceeds without a primary kinetic isotope effect ($k_H/k_D = 1.23 \pm 0.12$).[18] This figure seems low since the isomer distribution studies on the sulphonation of the 10π electron aromatic hydrocarbons revealed a substantial degree of steric hindrance for the α-substitution.[17] The reported figure may, however, be unreliable since the very limited information indicates that it was determined by the competitive method using mixtures of $C_{10}{}^1H_8$ and $C_{10}{}^2H_8$; it was pointed out that this method only leads to mechanistically significant results with substrates of low or moderate reactivity (see also later).[19] In view of the high reactivity of aromatic hydrocarbons towards sulphur trioxide, the kinetic isotope effects for hydrogen in the present study have all been determined using substrates which allow intramolecular protium–deuterium competition, *viz.* 1,2,4,5-tetramethyl[3-^{2}H]benzene, [1,4-$^2H_2$]naphthalene, and 1,6-methano[2,7-$^2H_2$][10]annulene.

RESULTS

The intramolecular substrate kinetic isotope effects in the sulphur trioxide sulphonation of the three hydrocarbons studied are given in Table 1. The isotopic composition of the unconverted substrate reveals that the hydrogen exchange during the reaction is relatively unimportant. Moreove: it will mainly occur between the acidic hydrogen of the arenesulphonic acid and the residual arene after the sulphonation has taken place. Thus it will not alter the isotopic composition of the aryl groups of the sulphonic acids which are far less reactive towards aryl hydrogen exchange than the corresponding hydrocarbons. Data for related substrates and reactions are listed for comparison. The primary substrate kinetic isotope effect is greater for sulphonation than for nitration and bromination.

DISCUSSION

The aprotic sulphonation of aromatic substrates with sulphur trioxide proceeds by the sequence (1)—(3). Applications of the steady-state treatment to the two σ-complexes leads to the rate equation (I). The various limiting conditions are specified in Table 2.

$$v_{ArS_2O_6H} = \frac{k_1k_2k_3[ArH][SO_3]^2}{k_{-1}(k_{-2} + k_3) + k_2k_3[SO_3]} \qquad (I)$$

For *trichlorofluoromethane* as solvent, the rate of sulphonation is first order in sulphur trioxide [4a] and apparently $k_{-1}(k_{-2} + k_3) \ll k_2k_3[SO_3]$, *i.e.* step (1) is

TABLE 2

Mechanistic extremes for the aprotic aromatic sulphonation by the steps (1)—(3)

Mechanistic limitations	Rate equation	Rate-limiting step	Primary substrate kinetic isotope effect of hydrogen: Intermolecular isotopic competition	Primary substrate kinetic isotope effect of hydrogen: Intramolecular isotopic competition
$k_{-1}(k_{-2} + k_3) \ll k_2k_3[SO_3]$; $k_{-2} \ll k_3$	$v = k_1[ArH][SO_3]$	1	No	No
$k_{-1}(k_{-2} + k_3) \ll k_2k_3[SO_3]$; $k_{-2} \gg k_3$	$v = k_1[ArH][SO_3]$	1	No	No *
$k_{-1}(k_{-2} + k_3) \gg k_2k_3[SO_3]$; $k_{-2} \ll k_3$	$v = (k_1k_2/k_{-1})[ArH][SO_3]^2$	2	No	No
$k_{-1}(k_{-2} + k_3) \gg k_2k_3[SO_3]$; $k_{-2} \gg k_3$	$v = (k_1k_2k_3/k_{-1}k_{-2})[ArH][SO_3]^2$	3	Yes	Yes

* See also the discussion.

rate limiting. Inter- and intra-molecular isotopic competition will thus never show a significant difference in rate between sulphodeprotonation and sulphodedeuteration. The sulphonation of naphthalene at position 1 with SO_3 in dichloroethane, which is considered to be a non-complexing solvent, proceeds in fact without an *inter*molecular primary kinetic isotope effect ($k_H/k_D = 1.23 \pm 0.12$).[18] The sulphonation of benzene [5] and 1,3,5-trimethylbenzene [9] proceeds without an *intra*molecular primary kinetic isotope effect. However, in contrast, there is a substantial *intra*molecular primary isotope effect with 1,2,4,5-tetramethylbenzene and naphthalene, illustrating that the description of the sulphonation of these highly reactive substrates in terms of the steps (1)—(3) is incomplete. The occurrence of the primary isotope effects with these reactive substrates infers that the distribution of SO_3 over the protium- and deuterium-carrying ring carbons has to take place after the rate-limiting step. It is proposed that with these highly reactive substrates the rate-limiting step is the formation of an ' encounter complex '.[20] The formation of this complex at the encounter rate leads to loss of substrate selectivity, but the positional selectivity will be retained.[21] The sulphonation of reactive substrates in CCl_3F is therefore thought to proceed by the steps (4), (5), (2) and (3). The energy profile for this process is shown as curve a in Figure 1.

$$ArH + SO_3 \underset{-4}{\overset{4}{\rightleftharpoons}} \text{encounter complex} \qquad (4)$$

$$\text{encounter complex} \underset{-5}{\overset{5}{\rightleftharpoons}} Ar\overset{+}{\underset{H}{\diagup\diagdown}}SO_3^- \qquad (5)$$

It is considered that the σ-complexes $HAr^+SO_3^-$ and $HAr^+S_2O_6^-$ are of similar π-electron energy content. An intramolecular primary kinetic isotope effect will now be observed, provided that (i) the free-energy content of the transition state for the formation of the first σ-complex from the ' encounter complex ' ($\Delta G^{\ddagger}_1$) is smaller than, or equal to, that for the intramolecular proton abstraction in the second σ-complex ($\Delta G^{\ddagger}_2$), and (ii) $k_{-2} \geqslant k_3$. The two step-process presented here leading to the (primary) σ-complex [steps (4) and (5)] is reminiscent to that for the fast electrophilic aromatic nitrations.[20,21]

The existence of an intramolecular primary kinetic isotope effect in the sulphonation in CCl_3F might also be explained in terms of the steps (1)—(3). The first σ-complex formed from ArH and SO_3 in the rate-limiting step (1) then has to allow redistribution of SO_3 over the various hydrogen- and deuterium-substituted carbons *via* an intermediate π-complex [steps (6) and (7)]. The necessary condition that this second step will have a low

$$Ar\overset{+}{\underset{SO_3^-}{\diagup\diagdown}}H \rightleftharpoons [ArH{\cdot}SO_3] \qquad (6)$$

$$[ArH{\cdot}SO_3] \rightleftharpoons Ar\overset{+}{\underset{SO_3^-}{\diagup\diagdown}}H \qquad (7)$$

free energy of activation relative to that of step (−1) renders such a mechanism unlikely.

It could be argued that the non-existence of an intermolecular primary kinetic isotope effect with naphthalene [18] might be due to problems of incomplete mixing.[22] However, the competative method applied for the naphthalene study gives for toluene and benzene as competitive substrates k_t/k_b values very different from unity, *viz.* ≃35.[5] In comparison with the mixed nitric acid nitrations [20] it is anticipated that with the more activated substrates 1,2,4,5-tetramethylbenzene and naphthalene the sulphonations approach the rate of encounter between the aromatic substrate and SO_3.

In conclusion, the aprotic sulphonation with non-complexing solvents of 1,2,4,5-tetramethylbenzene and naphthalene show significant intramolecular primary kinetic isotope effects of hydrogen. This may be

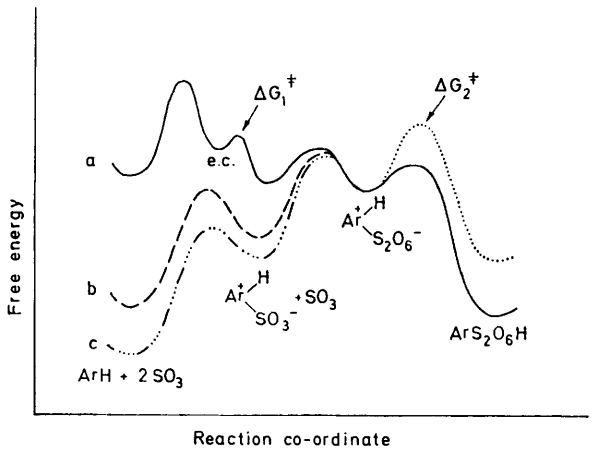

FIGURE 1 Energy profiles for the aprotic aromatic sulphonation with SO_3 in CCl_3F (a, ——; the encounter complex is indicated by e.c.), CH_3NO_2 (b, — —), and dioxan (c, — · · · · —) as solvent. The situation of steric hindrance for step (3) is also indicated (· · · · · ·).

explained in terms of the formation of the ' encounter complex ' as the rate-limiting step. With benzene [5] and 1,3,5-trimethylbenzene [9] there is no primary kinetic isotope effect, indicating that $k_{-2} \ll k_3$.

For *nitromethane* as complexing solvent, the rate of sulphonation is of the second order in sulphur trioxide [4b] and apparently $k_{-1}(k_{-2} + k_3) \gg k_2k_3[SO_3]$. With benzene [5] and 1,3,5-trimethylbenzene,[9] and allowing intramolecular hydrogen competition there is no primary substrate kinetic isotope effect and accordingly $k_{-2} \ll k_3$, *i.e.* step (2) is rate limiting. With 1,2,4,5-tetramethylbenzene and naphthalene there is a substantial intramolecular kinetic isotope effect, illustrating that $k_{-2} > k_3$ and that step (3) is now rate limiting.

With *dioxan* as solvent the behaviour is similar to that of nitromethane, but the complexation of SO_3 is stronger with dioxan than nitromethane.[23] With anthracene and 1,6-methano[10]annulene large kinetic isotope effects are observed, indicating step (3) to be rate limiting ($k_{-2} > k_3$).

The reaction profiles for the aprotic sulphonation in the three solvents are indicated in Figure 1. The

sulphonation proceeds *via* two σ-complexes as subsequent intermediates. The intermediacy of two subsequent σ-complexes was proposed before, *e.g.* in the electrophilic substitution of paracyclophanes [24] and aromatic sulphonation with concentrated sulphuric acid.[2c]

The absence of a kinetic isotope effect for the sulphonation of 1,3,5-trimethylbenzene is remarkable in view of (i) the presence of an (intermolecular) kinetic isotope effect for its bromination, and (ii) the internal strain which is present in the resulting pyrosulphonic acid. This is apparent from the relatively high rate of desulphonation of the corresponding sulphonic acid in aqueous sulphuric acid,[25] and which will be about equal to that of 2,6-dimethyl-t-butylbenzene which was estimated to be 17 kcal mol^{-1}.[26]

The occurrence of a kinetic isotope effect with 1,2,4,5-tetramethylbenzene may be explained in terms of additional steric hindrance for step (3), due to buttressing [27] of the two methyls *ortho* to the reaction centre by the adjacent methyls.

The intramolecular kinetic isotope effect for both the sulphonation and nitration is greater for the *meso*-substitution of anthracene than for the α-substitution of naphthalene. This reflects the higher degree of steric hindrance for step (3) with the former substitution due to the presence of the second *peri*-hydrogen adjacent to the reaction centre.

The enhanced steric requirements for sulphonation compared with nitration is confirmed by the larger kinetic isotope effect for the sulphonation as compared with the nitration of [1,4-$^2H_2$]naphthalene (Table 1).

The substantially larger kinetic isotope effect of 1,6-methano[10]annulene compared with naphthalene is ascribed to a lower rate of step (3) with the former substrate. It may be rationalized in terms of SO_3 attack from the bottom side of the annulene (*i.e. trans* to the methano-bridge), as the proton abstraction from C(2) of the resulting σ-complex will encounter steric hindrance from the methano-bridge.

EXPERIMENTAL

Materials.—1,2,4,5-Tetramethyl[3-^{2}H]benzene and 1,6-methano[2,7-$^2H_2$][10]annulene were synthesized from the corresponding 3-bromo- and 2,7-dibromo-derivatives respectively with butyl-lithium and subsequent reaction with deuterium oxide.[28] [1,4-$^2H_2$]Naphthalene was obtained from Merck, Sharp, and Dohme, Canada.

The isotopic composition of the aromatic hydrocarbons were determined by electron impact or field-ionization mass spectrometry using AEI MS-9 and Varian 711 MAT mass spectrometers. The accelerating voltage of the bombarding electrons was taken so low that there is just no $M - 1$ peak (for 1,2,4,5-tetramethylbenzene 12 eV, 1,6-methano-[10]annulene 9 eV, and naphthalene 15 eV).

Sulphonation Procedures.—The sulphonation procedures with sulphur trioxide for nitromethane [17a] and trichlorofluoromethane,[9] and for dioxan [10,17b] as solvent were described.

Deuterium Analysis of Arenesulphonic Acids.—The isotopic composition and the deuterium content of the arenesulphonate salts were determined by quantitative ^{1}H n.m.r. analysis of the solutions of the arenesulphonates in D_2O as solvent using Varian HA 100 and XL 100 spectrometers.

The spectrum of 2,3,5,6-$Me_4C_6HSO_3K$ in D_2O exhibits absorptions at δ 7.48 (s, 1 H, 4-H), 2.88 (s, 6 H, 2,6-Me_2), and 2.53 (s, 6 H, 3,5-Me_2). The [2,3,5,6-$Me_4C_6HSO_3^-$]/[[4-^{2}H]-2,3,5,6-$Me_4C_6HSO_3^-$] ratio was calculated from the ratio of the 7.48 signal to the sum of the 2.88 and 2.53 signals for the partially deuteriated relative to that of the non-deuteriated sulphonate salt (which was used as reference).

Sulphonation of [1,4-$^2H_2$]naphthalene leads mainly to α-substitution with formation of [4-^{2}H]- and [5,8-$^2H_2$]-naphthalene-1-sulphonic acid, the degree of β-substitution, leading to about equal amounts of [1,4-$^2H_2$]- and [5,8-$^2H_2$]-naphthalene-2-sulphonic acid, being small (Figure 2). The two 1-sulphonates give an absorption at δ 8.28 (d, 1 H, 2-H), whereas the signal at 8.90 (d, 1 H, 8-H) is only due to the [5,8-$^2H_2$]-1-sulphonate. The ratio of the [4-^{2}H]- and

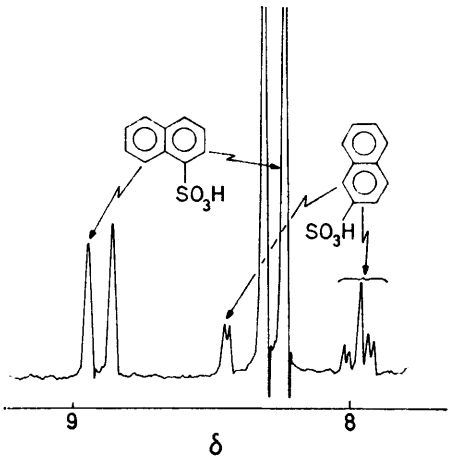

FIGURE 2 Low-field ^{1}H n.m.r. absorption of the sulphonate mixture obtained on sulphonation of [1,4-$^2H_2$]naphthalene with SO_3 in nitromethane at 0 °C

[5,8-$^2H_2$]-1-sulphonate was calculated from the intensity ratio of the signals at 8.28 and 8.90.

Sulphonation of 1,6-methano[2,7-$^2H_2$][10]annulene leads exclusively to α-substitution with formation of [7-^{2}H]- and [5,10-$^2H_2$]-2-sulphonic acid. In the ^{1}H n.m.r. spectrum of the sulphonate mixture two absorptions are relevant, *viz.* at 8.44 {d, 1 H, 10-H of [7-^{2}H]-2-sulphonate} and 8.20 {d, 1 H, 3-H of both [7-^{2}H]- and [5,10-$^1H_2$]-2-sulphonate}.

The ratio of the two 2-sulphonates was calculated from the ratio of these signals.

Calculation of the Kinetic Isotope Effect.—The kinetic isotope effect of hydrogen, k_H/k_D, was calculated from the ratio of the different isotopically labelled sulphonates. Corrections were made for the presence of small amounts of differently deuterium labelled substrate molecules under the assumption that these molecules react equally as fast as the others (*viz.* by encounter control).

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