

**Arylsulfonylation of Aromatic Compounds. III.**  
**Kinetics of the Nitrophenylsulfonylation of Alkylbenzenes<sup>1a-c</sup>**

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The *m*- and *p*-nitrophenylsulfonylation of alkylbenzenes in ethyl acetate solution is first order in peroxide and is not acid catalyzed. Although simple first-order kinetics with respect to alkylbenzenes are observed, with benzene itself the reaction first order with respect to arene competes with a reaction of the peroxide which is zero order with respect to the aromatic. In methylene chloride, arylsulfonylation gives simple first-order kinetics with respect to benzene as well as toluene and ethylbenzene. In ethyl acetate, the relative reactivities of the alkylbenzenes with respect to benzene are in good agreement with those previously reported from competitive reactions. The rates with benzene and hexadeuteriobenzene are identical; therefore, carbon-hydrogen bond breaking is not rate determining. Mesitylene is 1350 times as reactive as benzene for *p*-nitrophenylsulfonylation; therefore,  $\pi$ -complex formation is not rate determining. The energies of activation for *p*- and *m*-nitrophenylsulfonylation calculated from the pseudo-first-order rate constants are, respectively, benzene, 18, 17 (corrected for the competing solvolytic reaction); toluene, 15.9, 15.7; ethylbenzene, 16.2, 16.1; isopropylbenzene, 15.8, 15.8; *tert*-butylbenzene, 16.1, 16.0; *p*-xylene, 13.9, 14.9; and mesitylene, 12.8, 13.8.

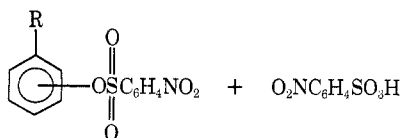
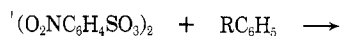
The arylsulfonylation of aromatic nuclei has been tentatively classified as an electrophilic substitution for several reasons. First, the partial rate factors for the halobenzenes and alkylbenzenes are appropriate for an electrophilic but not a homolytic reaction. Second, there is a complete absence of side-chain reaction with the alkylbenzenes characteristic of free-radical processes.<sup>1b</sup> Third, no esr signal could be obtained using a reacting mixture of sulfonyl peroxide and benzene.<sup>2</sup>

In the preceding paper of this series,<sup>1b</sup> relative reactivities, orientations of substitution, and partial rate factors were determined for the *o*- and *m*-nitrophenylsulfonylation of toluene, ethylbenzene, cumene, and *tert*-butylbenzene. The relative reactivities were obtained from a competitive substitution by the peroxide of a mixture of benzene and the alkylbenzene.

Arylsulfonylation can readily be followed kinetically because the decrease in the peroxide content of the reaction mixture can be measured by iodometric titration. The present kinetic study was undertaken to determine, first, the order of the substitution with respect to the peroxide; second, whether the reaction is acid catalyzed; third, the order of the reaction with respect to arene; fourth, the relative reactivities of benzene, toluene, ethylbenzene, cumene, and *tert*-butylbenzene; fifth, whether the rate-determining step is the breaking of the carbon-hydrogen bond; sixth, whether  $\pi$ -complex formation is rate determining; and, seventh, the dependence of the enthalpy and entropy of activation on the nature of the alkyl group in the substrate and the orientation of the nitro group in the peroxide.

**Results and Discussion**

**Selection of the Isomeric Nitrobenzenesulfonyl Peroxides.**—In the preceding paper of this series, *o*- and *m*-nitrobenzenesulfonyl peroxides were used in the substitution of alkylbenzenes. In the present work it was decided to abandon the use of *o*-nitrobenzenesulfonyl peroxide for several reasons. First, it is the least stable of the three isomeric peroxides; second, the nitro group may confer unusual steric influence when ortho to the reaction site; and, third, since the esters of the ortho acid needed as reference standards for glpc analyses in some of the planned future work are the lowest melting of the isomers, they are most difficult to obtain in pure state. The meta peroxide is more de-



(1) (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1968, Abstract No. S113. Taken in part from the Ph.D. Thesis of J. E. Gagen, Case Western Reserve University, 1967. (b) For the previous paper of this series, see R. L. Dannley, J. E. Gagen, and O. J. Stewart, *J. Org. Chem.*, **35**, 3076 (1970). (c) Supported in part by the U. S. Army Research Office (Durham) through Grant No. DA-ARO-(D)-31-124-G42. (d) NASA Trainee, 1965-1967.

(2) R. L. Dannley and G. E. Corbett, *J. Org. Chem.*, **31**, 153 (1966).

sirable in that it is the most stable of the three peroxides, and the corresponding acid chloride used in its synthesis is the lowest priced of the isomeric chlorides. Unfortunately, the esters of the meta acid are not much higher melting than those of the ortho acid. The para peroxide has as its principal advantage the fact that, as its reference esters needed for glpc analyses are the highest melting of all the isomers, they can be prepared most easily in a high state of purity. Therefore both the meta and para peroxides have some desirable attributes, and these two were used in the present work.

**Order with Respect to Sulfonyl Peroxide.**—Most of the kinetic experiments in this work were performed in ethyl acetate solution. In every case, with both peroxides, a good first-order plot was generally obtained for the disappearance of the sulfonyl peroxide through at least 2 half-lives. Occasionally there was a slight decrease in rate in the succeeding half-lives and, at the very highest temperatures used, poor first-order plots were sometimes secured. The rates were very reproducible with a particular sample of peroxide, usually within 1% and with maximum 3% differences from mean values. Deviations of 10% from average values were obtained occasionally between several investigators using different samples of peroxide, solvent, substrates, etc.

**Absence of Acid Catalysis.**—The absence of any autocatalysis is an indication that the substitution is not acid catalyzed, for the concentration of the corresponding nitrosulfonic acid rises from zero to appreciable concentrations during the course of the peroxide disappearance. However, Levi, Kovacic, and Gormish<sup>3</sup> have recently reported that aluminum chloride can catalyze the decomposition of *m*-nitrobenzenesulfonyl peroxide in an acetonitrile solution of toluene, and so acid catalysis might be expected.

It has been found in the present work, however, that the rate ( $k = 4.77 \times 10^{-5} \text{ sec}^{-1}$ ) of reaction of *p*-nitrobenzenesulfonyl peroxide (0.01 *M*) with benzene (0.50 *M*) in ethyl acetate solution at 20° with no *p*-nitrobenzenesulfonic acid added is actually slightly greater than the rate ( $k = 3.92 \times 10^{-5} \text{ sec}^{-1}$ ) with 10 mol of the acid added per mole of peroxide. The absence of catalysis by the sulfonic acid in ethyl acetate may be due to the basicity of this solvent which permits its protonation in preference to the peroxide.

**The Order of the Reaction with Respect to Arene.**—The pseudo-first-order rate constants given in Table I are based on the rate of disappearance of the peroxide and assume that the arene concentrations are large enough to remain unchanged during the reaction. In the few experiments in which the molarity of the arene was low enough to be appreciably decreased during the course of the reaction, second-order rate constants involving the arene concentration were calculated and then converted into first-order rate constants dependent only on the peroxide concentration (Table I footnote). The differences between the pseudo-first-order rate constants obtained by the two methods of calculation were too small to have any influence on the following discussion. From the pseudo-first-order rates for *p*-nitrophenylsulfonylation, first-order dependencies were obtained with respect to toluene (0.98) and

TABLE I  
DEPENDENCE OF THE PSEUDO-FIRST-ORDER RATE OF REACTION OF A NITROBENZENESULFONYL PEROXIDE (0.01 *M*) UPON AN ARENE CONCENTRATION IN ETHYL ACETATE SOLUTION

Arene	[Arene], <i>M</i>	$k \times 10^5$ , $\text{sec}^{-1}$	<i>T</i> , °C
<i>m</i> -Nitrophenylsulfonylation			
Benzene	0.50	1.49	10
Benzene	1.00	2.63	10
Benzene	1.50	3.96	10
Benzene	0.25	3.34	20
Benzene	0.50	5.33	20
Benzene	1.00	8.65	20
Benzene	1.50	12.3	20
Benzene	0.25	13.74	30
Benzene	0.50	17.3	30
Benzene	0.75	22.4	30
<i>p</i> -Nitrophenylsulfonylation			
Benzene	0.50	1.22	10
Benzene	0.75	1.58	10
Benzene	1.00	2.06	10
Benzene	0.25	3.53	20
Benzene	0.50	4.77	20
Benzene	1.00	6.70	20
Benzene	2.00	10.45	20
Benzene	0.20	9.16	30
Benzene	0.50	13.1	30
Benzene	1.00	20.5	30
Toluene	0.10	6.99 <sup>a</sup>	15
Toluene	0.23	14.5	15
Toluene	0.36	23.4	15
Toluene	0.50	33.0	15
<i>p</i> -Xylene	0.10	5.15 <sup>a</sup>	-15
<i>p</i> -Xylene	0.23	10.9	-15
<i>p</i> -Xylene	0.36	19.9	-15
<i>p</i> -Xylene	0.50	26.8	-15

<sup>a</sup> Second-order ( $k[\text{P}][\text{Ar}]$ ) calculations were also performed because the initial arene molarities were so small that these arene concentrations decreased appreciably during the course of the reaction. The resultant second-order constants were converted into pseudo-first-order rate constants: toluene, 7.25; *p*-xylene,  $5.34 \times 10^{-5} \text{ sec}^{-1}$ .

*p*-xylene (1.05). However, for benzene the order is 0.66 for *p*-nitrophenylsulfonylation and 0.70 for *m*-nitrophenylsulfonylation. These partial orders with respect to benzene are dependent on the solvent (ethyl acetate) because in methylene chloride, the *p*-nitrophenylsulfonylation (Table II) of both benzene (0.94) and toluene (1.01) is first order with respect to arene.

In ethyl acetate the apparent fractional order is obtained because there are two competing reactions. The observed pseudo-first-order rate ( $k_1[\text{P}]$ ) with benzene is the sum of a first-order ( $k_2[\text{P}]$ ) dissociation to a reactive species plus a bimolecular nucleophilic displacement ( $k_3[\text{P}][\text{B}]$ ) by the arene on an oxygen of the peroxide (eq 1). Thus from a plot of the observed  $k_1$ , against

$$-\frac{d[\text{P}]}{dt} = k_1[\text{P}] = k_2[\text{P}] + k_3[\text{P}][\text{B}] \quad (1)$$

the concentration of benzene, the slope provides the rate constant of the bimolecular reaction ( $k_3$  for the *p*-nitrophenylsulfonylation at 20° is  $3.9 \times 10^{-5}$ ; for *m*-nitrophenylsulfonylation at 20° is  $7.1 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ ) and the intercept at zero concentration of benzene is the pseudo-first-order rate constant for the dissociation zero order with respect to benzene ( $k_2$  at

(3) E. M. Levi, P. Kovacic, and J. E. Gormish, private communication.

TABLE II

DEPENDENCE OF THE PSEUDO-FIRST-ORDER RATE OF REACTION OF *p*-NITROBENZENESULFONYL PEROXIDE (0.01 *M*) WITH AN ARENE IN METHYLENE CHLORIDE SOLUTION

Arene	[Arene], <i>M</i>	$k \times 10^5$ , sec <sup>-1</sup>	<i>T</i> , °C
Benzene	0.25	3.07 <sup>a</sup>	20
Benzene	0.50	6.07 <sup>a</sup>	20
Benzene	1.00	11.4 <sup>a</sup>	20
Benzene	2.00	21.7 <sup>a</sup>	20
Toluene	0.10	20.4 <sup>b</sup>	15
Toluene	0.23	47.6 <sup>b</sup>	15
Toluene	0.36	72.2 <sup>b</sup>	15
Toluene	0.50	14.2	-5
Toluene	0.50	39.1	5
Toluene	0.50	108. <sup>b</sup>	15
Toluene	0.50	172. <sup>c</sup>	20
Ethylbenzene	0.50	13.2	-5
Ethylbenzene	0.50	37.4	5
Ethylbenzene	0.50	108.	15
Ethylbenzene	0.50	175. <sup>c</sup>	20

<sup>a</sup> These rates yield a 0.94 order with respect to benzene.

<sup>b</sup> These rates yield a 1.01 order with respect to toluene. <sup>c</sup> These rates obtained by extrapolation from the rates at lower temperatures.

20° for *p*-nitrophenylsulfonoxylation is  $2.7 \times 10^{-5}$ ; for *m*-nitrophenylsulfonoxylation is  $1.7 \times 10^{-5}$  sec<sup>-1</sup>).

**Relative Reactivities of the Arenes.**—Relative reactivities of arenes in aromatic substitutions are traditionally obtained by comparing the rates with various arenes to a similar rate with benzene. In the present work benzene is obviously a poor reference compound for its substitution is unique among the arenes here studied inasmuch as it results from two competing reactions. However, to permit correlations with the published data for other aromatic substitutions, it was decided to conform to tradition and use benzene as a reference material. This decision necessitated a choice of whether to use as the reference the overall pseudo-first-order rate constant ( $k_1$ ) with benzene or the rate constant ( $k_2$ ) for the second-order reaction. The selection of  $k_1$  as the reference value has the advantage that it permits comparisons of kinetic relative reactivities with relative reactivities based on competitive reactions.

Using the overall pseudo-first-order rate constant ( $k_1$ ) becomes more appropriate by comparing only those rates measured or extrapolated for a 1 *M* arene concentration. For the *m*-nitrophenylsulfonoxylation of these hydrocarbons, relative reactivities were previously determined<sup>1b</sup> by glpc of the products of the substitutions in competitive reactions. With toluene, ethylbenzene, and *tert*-butylbenzene at least one competitive determination was available for the 1.0 *M* arene solution, and these are the values listed in Table III. The only available figures with cumene were obtained in neat mixtures of the arene and benzene, and therefore the value listed is not completely valid for comparison. In all cases, however, the relative reactivities obtained by competitive means differ at most by 20% from the kinetic values based on  $k_1$  for benzene. Invariably the kinetic relative reactivity listed for an alkylbenzene is larger than the competitive relative reactivity value. The use of  $k_2$  for benzene instead of  $k_1$  would make this difference even greater. In future work, kinetic determinations with some substrates may not be feasible and competi-

TABLE III

PSEUDO-FIRST-ORDER RATE CONSTANTS (SEC<sup>-1</sup>) AND RELATIVE REACTIVITIES AT 20° FOR THE REACTION OF *m*- AND *p*-NITROBENZENESULFONYL PEROXIDES (0.01 *M*) WITH ARENES (1.0 *M*) IN ETHYL ACETATE

	<i>m</i> -Nitrophenylsulfonoxylation			<i>p</i> -Nitrophenylsulfonoxylation	
	$k \times 10^5$	$k_{Ar}/k_B$ , kinetic	$k_{Ar}/k_B$ , competitive	$k \times 10^5$	$k_{Ar}/k_B$ kinetic
Benzene	8.65	1.0	1.0	6.70	1.0
Toluene	172	19.9	19.0	121.8	18.2
Ethylbenzene	174 <sup>a</sup>	20.0	16.7	87.3 <sup>c</sup>	13.0
Cumene	144 <sup>a</sup>	16.6	13.5 <sup>b</sup>	89.4 <sup>a</sup>	13.3
<i>tert</i> -Butylbenzene	131 <sup>a</sup>	15.1	13.2	82.0 <sup>a</sup>	12.2
<i>p</i> -Xylene	2960 <sup>c</sup>	340	...	1400 <sup>c</sup>	200
Mesitylene	20,300 <sup>d</sup>	2400	...	9000 <sup>d</sup>	1350

<sup>a</sup> Calculated values from 0.5 *M* rates using a 0.98 order for the arene. <sup>b</sup> A neat mixture of cumene-benzene. <sup>c</sup> Calculated from 0.5 *M* rate at lower temperatures using 1.05 order for the arene. <sup>d</sup> Calculated from 0.5 *M* rate at lower temperatures using 1.00 order for the arene.

tive determinations of relative reactivities might be the only ones available. Therefore, the use of  $k_1$  for benzene as a reference standard seems the most attractive for it should lead to a more homogeneous volume of data. The significance of these relative reactivities has been discussed previously.<sup>1b</sup>

A change in solvent may, of course, affect relative reactivity of substrates. Because arylsulfonoxylation in methylene chloride is first-order with both benzene and alkylbenzenes, relative reactivities were obtained in this solvent for the *p*-nitrophenylsulfonoxylation of benzene (1.0), toluene (29.7), and ethylbenzene (29.7). Surprisingly, although both toluene and ethylbenzene have larger relative reactivities (which should indicate a higher specificity of the reagent) in methylene chloride than in ethyl acetate, the two alkylbenzenes have identical relative reactivities (indicating a low specificity) in the chlorinated solvent. Further work is needed to explain these anomalous effects in methylene chloride.

**Partial Rate Factors.**—Traditionally, relative reactivities are used to calculate partial rate factors. The same inherent errors (competitive reactions, etc.) are usually encountered with both the kinetic and competitive determinations of relative reactivity. The kinetic method is most reproducible in sulfonoxylations because of the precision of the titrations. In Table IV are listed partial rate factors for the *m*-nitrophenylsulfonoxylation of the arenes calculated from both competitive and kinetic relative reactivities using  $k_1$  for benzene as a standard. At the present level of sophistication in the analysis of the mechanism of aromatic substitution, either set of values is probably suitable. The significance of these values has already been discussed.<sup>1b</sup>

**Carbon-Hydrogen Bond Breaking as a Rate-Determining Step.**—The rates of reaction of *p*-nitrobenzenesulfonyl peroxide with benzene ( $4.77 \times 10^{-5}$  sec<sup>-1</sup>) and hexadeuteriobenzene ( $4.78 \times 10^{-5}$  sec<sup>-1</sup>) were identical within experimental limits. Therefore, arylsulfonoxylation is similar to most nitrations, halogenations, and Friedel-Crafts reactions in that carbon-hydrogen bond breaking is not rate determining.

TABLE IV  
PARTIAL RATE FACTORS CALCULATED FROM KINETIC AND  
COMPETITIVE RELATIVE REACTIVITIES FOR THE  
*m*-NITROPHENYLSULFONOXYLATION OF ALKYL BENZENES

	Partial Rate Factors from	
	Kinetic $k_{Ar}/k_B$	Competitive $k_{Ar}/k_B$
Toluene		
Ortho	19.0	18.1
Meta	2.1	2.0
Para	77.3	73.8
Ethylbenzene		
Ortho	18.9	15.8
Meta	2.8	2.3
Para	83.1	69.4
Cumene		
Ortho	11.7	9.5
Meta	3.2	2.6
Para	69.7	56.7
<i>tert</i> -Butylbenzene		
Ortho	3.0	2.6
Meta	7.4	6.5
Para	61.0	53.3

**$\pi$ -Complex Formation.**—For the *p*-nitrophenylsulfonoxylation of polyalkylbenzenes the relative reactivities with respect to benzene (Table III) are, *p*-xylene, 200; mesitylene, 1350. For *m*-nitrophenylsulfonoxylation the values are, *p*-xylene, 340; mesitylene, 2400. These high values are, characteristic of substitutions in which  $\pi$ -complex formation is not rate determining. In the reaction of nitration using nitronium tetrafluoroborate in tetramethylenesulfone solution where  $\pi$ -complex formation is rate determining, the relative reactivities are, *p*-xylene, 1.96; mesitylene, 2.71.<sup>4</sup>

**Reaction Parameters.**—From the rate constants ( $k_1$ ) for benzene in Table I, the  $k_2$  and  $k_3$  values in Table VII were obtained. From these rate constants and those in Tables V and VI, the activation parameters (Table VIII) were calculated. The derivation of  $k_2$  and  $k_3$  for benzene from the measured rate constants ( $k_1$ ) reduces precision so that the parameters derived from these  $k_2$  and  $k_3$  values are of very limited accuracy.

The relationships of the parameters for *m*-nitrophenylsulfonoxylation and *p*-nitrophenylsulfonoxylation in general are very similar, and the following discussion is applicable to both substitutions. The reaction parameters for all of the monoalkylbenzenes are essentially identical. As expected, the enthalpies of activation for *p*-xylene and mesitylene are appreciably smaller than those for the monoalkylbenzenes, and these two polyalkylbenzenes also have entropies of activation with somewhat larger negative values (indicating possibly greater ionic character of their transition states). The enthalpies of activation for benzene substitution derived from the  $k_3$  values (reaction first order with respect to benzene) are similar to those for the monoalkylbenzenes, but the lack of precision prevents more definitive comparisons.

The competing reaction for benzene substitution which is zero order with respect to benzene was first considered to consist of a rate-determining solvolytic ionization of the peroxide into some type of ion pair. Despite the limited accuracy of the  $k_2$  values, it is

TABLE V  
TEMPERATURE DEPENDENCE OF THE PSEUDO-FIRST-ORDER RATE  
CONSTANTS FOR THE DISAPPEARANCE OF  
*m*-NITROBENZENESULFONYL PEROXIDE (0.01 *M*) IN ARENES  
(0.5 *M*) IN ETHYL ACETATE SOLUTION

Arene	<i>T</i> , °C	$k \times 10^3$ , sec <sup>-1</sup>
Benzene	10.00	1.49
Benzene	20.00	5.33
Benzene	30.00	17.3
Benzene	40.00	55.0
Toluene	-10.0	4.01
Toluene	-0.1	12.3
Toluene	10.05	34.3
Toluene	20.10	87.2
Ethylbenzene	0.00	10.93
Ethylbenzene	10.00	30.9
Ethylbenzene	20.00	81.6
Cumene	0.00	9.95
Cumene	10.00	27.5
Cumene	20.00	73
<i>tert</i> -Butylbenzene	0.00	8.85
<i>tert</i> -Butylbenzene	10.00	25.1
<i>tert</i> -Butylbenzene	20.00	66.4
<i>p</i> -Xylene	-33.3	4.99
<i>p</i> -Xylene	-20.05	25.7
<i>p</i> -Xylene	-10.0	79.3
Mesitylene	-39.8	24.0
Mesitylene	-33.3	54.3
Mesitylene	-25.0	141

TABLE VI  
TEMPERATURE DEPENDENCE OF THE PSEUDO-FIRST-ORDER RATE  
CONSTANTS FOR THE DISAPPEARANCE OF  
*p*-NITROBENZENESULFONYL PEROXIDE (0.01 *M*) IN ARENES  
(0.5 *M*) IN ETHYL ACETATE SOLUTION

Arene	<i>T</i> , °C	$k \times 10^3$ , sec <sup>-1</sup>
Benzene	10.00	1.22
Benzene	20.00	4.77
Hexadeuteriobenzene	20.00	4.78
Benzene	30.00	15.6
Benzene	40.00	49.7
Toluene	0.00	8.32
Toluene	10.00	23.5
Toluene	20.00	61.7
Ethylbenzene	0.00	7.02
Ethylbenzene	10.00	20.7
Ethylbenzene	20.00	53.9
Cumene	0.00	6.16
Cumene	10.00	17.6
Cumene	20.00	45.3
<i>tert</i> -Butylbenzene	0.00	5.42
<i>tert</i> -Butylbenzene	10.00	15.9
<i>tert</i> -Butylbenzene	20.00	41.6
<i>p</i> -Xylene	-33.3	3.34
<i>p</i> -Xylene	-15.00	26.8
<i>p</i> -Xylene	-10.00	44.6
Mesitylene	-33.3	34.2
Mesitylene	-25.0	88.3
Mesitylene	-20.05	141

obvious that the enthalpies of activation for this process are much higher than those derived from the  $k_3$  figures. For the two reactions to compete, the entropies of activation for the  $k_2$  process must be much more positive (measured value  $30 \pm 4$  eu) than for the  $k_3$  reaction ( $-22$  eu). Such a large positive entropy of activation is not consistent with an ionization step but is more characteristic of a radical reaction. Obviously, if the reaction is a chain radical process, a good free-radical

(4) G. A. Olah, S. J. Kuhn, and S. Flood, *J. Amer. Chem. Soc.*, **83**, 4571 (1961).

TABLE VII  
 $k_2$  AND  $k_3$  FOR THE ARYLSULFONOXYLATION OF BENZENE

$T, ^\circ\text{C}$	$k_2 \times 10^5$ , mol l. <sup>-1</sup> sec <sup>-1</sup>	$k_3 \times 10^6$ , sec <sup>-1</sup>
<i>m</i> -Nitrophenylsulfonoxylation		
10	0.21	2.47
20	1.65	7.07
30	9.02	17.3
<i>p</i> -Nitrophenylsulfonoxylation		
10	0.35	1.68
20	2.7	3.86
30	6.1	14.2

TABLE VIII  
 ACTIVATION PARAMETERS FOR THE  
 NITROPHENYLSULFONOXYLATION OF ARENES IN ETHYL ACETATE

Arene	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal deg <sup>-1</sup> mol <sup>-1</sup>	$E_a$ , kcal mol <sup>-1</sup>	Log $A$
<i>m</i> -Nitrophenylsulfonoxylation				
Benzene <sup>a</sup>	20.6	-7.8	21.1	11.3
Benzene <sup>b</sup>	32 ± 1	+30 ± 4	31 ± 1	19
Benzene <sup>c</sup>	16 ± 0.5	-22	17	8.2
Toluene	15.2	-20.7	15.7	8.7
Ethylbenzene	15.5	-20.0	16.1	8.8
Cumene	15.3	-20.7	15.8	8.7
<i>tert</i> -Butylbenzene	15.5	-20.3	16.0	8.8
<i>p</i> -Xylene	14.4	-22.3	14.9	9.3
Mesitylene	13.3	-22.2	13.8	9.3
<i>p</i> -Nitrophenylsulfonoxylation				
Benzene <sup>a</sup>	21.2	-6.2	21.7	11.9
Benzene <sup>d</sup>	...	...	...	...
Benzene <sup>c</sup>	16 ± 2	-18	16 ± 2	9.4
Toluene	15.4	-20.8	15.9	8.7
Ethylbenzene	15.6	-20.1	16.2	8.8
Cumene	15.3	-21.6	15.8	8.5
<i>tert</i> -Butylbenzene	15.6	-20.6	16.1	8.7
<i>p</i> -Xylene	13.4	-22.6	13.9	8.2
Mesitylene	12.3	-22.4	12.8	8.2

<sup>a</sup> From the pseudo-first-order rate constants ( $k_1$ ). <sup>b</sup> From the reaction constants ( $k_2$ ) calculated for the reaction whose rate is independent of the benzene concentration. <sup>c</sup> From the reaction constants ( $k_3$ ) calculated for the reaction first order with respect to benzene concentration. <sup>d</sup> The  $k_2$  values were not reproducible enough to justify additional calculations.

inhibitor should eliminate it. Unfortunately most inhibitors (thiols, hydroquinone, etc.) react directly with the peroxide or are so highly colored (galvinoxyl, etc.)

that they interfere with the kinetic measurements. The alkylbenzenes are quite good radical traps, and the clean first orders observed with these hydrocarbons may be partially due to this attribute but their greater reactivity toward nuclear substitution is probably sufficient in itself to eliminate the competitiveness of any solvolytic process.

An enthalpy (21.4 kcal mol<sup>-1</sup>) and an entropy (-5.1 cal deg<sup>-1</sup> mol<sup>-1</sup>) of activation for the *m*-nitrophenylsulfonoxylation of benzene in ethyl acetate have recently been reported<sup>5</sup> corresponding to the value derived from  $k_1$  for the reaction.

**Summary.**—All of these data (except for the  $k_2$  reactions with benzene) are consistent with an electrophilic aromatic substitution in which the reaction of the peroxide with the aromatic substrate to form a  $\sigma$  complex is rate determining.

### Experimental Section

**Materials.**—The nitrobenzenesulfonyl peroxides, benzene, toluene, ethylbenzene, cumene, *tert*-butylbenzene and ethyl acetate were prepared or purified as described in the previous paper.<sup>1b</sup> Mesitylene (Matheson Coleman and Bell practical grade) was purified by glpc using a 20 ft × 3/8 in. SE-30 column using an Aerograph Model 1525-B chromatograph. *p*-Xylene (J. T. Baker reagent grade) was distilled through a 24-ft Vigreux column collecting a fraction with bp 136°. Hexadeuteriobenzene (Merck Sharp and Dohme) was used without purification.

**Typical Kinetic Procedure.**—*p*-Nitrobenzenesulfonyl peroxide (302.9 mg, 0.745 mol) was placed in a 100-ml reaction vessel in a constant-temperature bath (20 ± 0.05°), and ethyl acetate (50 ml) equilibrated to this temperature was added. Benzene (2.93 g, 0.0375 mol) was weighed into a 25-ml volumetric flask and diluted to the mark with ethyl acetate; the vessel was placed in the bath. After 10 min the solutions had equilibrated and were mixed. An aliquot (5 ml) was removed immediately (zero time) and titrated.

**Registry No.**—*m*-Nitrophenylsulfonyl peroxide, 6209-71-8; *p*-nitrophenylsulfonyl peroxide, 6209-72-9; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; *tert*-butylbenzene, 98-06-6; *p*-xylene, 106-42-3; mesitylene, 108-67-8; hexadeuteriobenzene, 1076-43-3.

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(5) J. Bolte, G. Dauphin, and A. Kergomard, *Bull. Soc. Chim. Fr.*, 2291 (1970).