Tetrahedron, 1963, Vol. 19, pp. 323 to 334. Pergamon Press Ltd. Printed in Northern Ireland

MECHANISM OF AROMATIC ALKYLATION—V

KINETICS OF THE REACTION BETWEEN BENZENIC HYDROCARBONS WITH SUBSTITUTED BENZYL BENZENESULPHONATES[1]

VIORICA IOAN, D. SĂNDULESCU, S. TITEICA and C. D. NENITZESCU
Chemical Institute of the R.P.R. Academy, Bucharest

(*Received* 10 *August* 1962)

Abstract—Kinetic measurements on the alkylation reaction of mesitylene and pentamethylbenzene with *p*-chlorobenzyl and *m*-nitrobenzyl benzenesulphonates were performed, under the catalytical action of benzenesulphonic acid in dichloroethane. It was established that in the rate equation the concentration of the sulphonic ester enters at the first power and the concentration of the acid catalyst at the second power, while the aromatic hydrocarbon is involved in a more complicated function. Starting from the idea that for the ionization of the benzenesulphonic ester two molecules of acid are necessary, one of which serves for solvation of the anion and the other for solvation of the cation, and that these two thus solvated ions remains bound as an ion pair in a cage of solvent molecules, a kinetic equation is established, in which the reaction rate appears as a hyperbolic function of the concentration of the aromatic hydrocarbon. This equation accounts well for the experimental facts.

THE quantitative study of Friedel-Crafts alkylation reactions of the aromatic nucleus presents experimental difficulties owing to the strong Lewis acids such as $AlCl_3$, $GaCl_3$, $SbCl_5$, etc. used as catalysts which are sensitive to moisture and only a few inert solvents are available for these catalysts. Because of the limited solubility of Friedel-Crafts catalysts, many reactions of this type proceed as heterogeneous reactions. Besides, the necessity of working in non-polar media with small solvation power for ions, leads to the formation of complex combinations and of molecular associations among the various species that take part as starting materials, intermediates, or reaction products; this greatly complicates the reaction kinetics.

A more simple alkylation reaction has been sought so as to avoid unfavourable secondary phenomena that develop in dilute solutions, and one which would serve as a model for a normal Friedel-Crafts alkylation reaction. Such a reaction seemed to be the condensation of benzyl benzenesulphonates and of derivatives substituted at the benzyl group with aromatic hydrocarbons, according to Földi:[2]

$$C_6H_5—CH_2{\cdot}O{\cdot}O_2S—C_6H_5 + C_6H_6 \rightarrow C_6H_5—CH_2—C_6H_5 + HO_3S—C_6H_5$$

The reaction proceeds almost quantitatively if the solution is sufficiently dilute. Qualitative tests indicated the generality of the reaction: it can be extended to the esters of a great number of secondary and even primary alcohols.[3,4]

The first attempts[5] showed that this reaction is catalysed by benzenesulphonic acid and consequently has an autocatalytic character. In the presence of weak bases such as calcium carbonate or dioxan, the reaction is completely inhibited.

---

[1] Part IV: V. Ioan, L. Teodorescu, S. Titeica and C. D. Nenitzescu, *Acad. R.P.R., Studii si Cercetari de Chim.* **7**, 355 (1959).

[2] Z. Földi, *Ber. Dtsch. Chem. Ges.* **61**, 1609 (1928).

[3] C. D. Nenitzescu, V. Ioan and L. Teodorescu, *Chem. Ber.* **90**, 585 (1957).

[4] W. J. Hickinbottom and N. W. Rogers, *J. Chem. Soc.* 4124 (1957); N. G. Rule and W. J. Hickinbottom, *Ibid.* 2509, 2517 (1959); M. S. Grant and W. J. Hickinbottom, *Ibid.* 2520 (1959).

In previous papers[5] kinetic determinations with a series of benzyl benzenesulphonates substituted in the benzyl group were made, the aromatic hydrocarbon, benzene, toluene or *m*-xylene being used as solvent. Measurements at various temperatures were taken, and activation energies and entropies determined.[5] In all cases studied the reaction proved to be of first order in benzenesulphonic ester and of second order in benzenesulphonic acid:

$$v = k[C_6H_5 \cdot SO_3 \cdot CH_2Ar][C_6H_5 \cdot SO_3H]^2$$

The remarkable bimolecularity of the acid catalyst in reactions of this type is general, as the same kinetics is also found in the aromatic alkylation with benzyl fluorides, chlorides and bromides under the action of benzenesulphonic acid in hydrocarbon media.[6,7] Measurements made for establishing the influence of association phenomena on the rate equation show that the observed exceptions, namely the decrease of the apparent rate constant with the increase of the concentration of benzyl benzenesulphonate is explained quantitatively and exactly enough by the association of this ester with benzenesulphonic acid.[8]

Scope and reaction conditions

In the present paper the kinetical order of the aromatic hydrocarbon in the alkylation reaction of the aromatic nucleus has been determined. Although the 1,2-dichloroethane used as solvent has a higher dielectric constant (D = 10·1) than aromatic hydrocarbons, it may be compared with these owing to its low power to solvate ions.

A difficulty encountered in working with relatively small concentrations of aromatic hydrocarbons in dichloroethane solution is the self-alkylation of the alkylating agent. Thus, with benzyl benzenesulphonate, a self-alkylation product $(C_7H_6)_X$ is obtained together with the alkylation product of the aromatic hydrocarbon. Consequently, *p*-chlorobenzyl and *m*-nitrobenzyl benzenesulphonate, in which the reactivity of the free positions from the benzylic ring is sufficiently diminished were used, thus practically avoiding the danger of self-alkylation.

The necessity of working with *p*-chloro- and *m*-nitrobenzyl benzenesulphonates which are less reactive than the unsubstituted benzyl benzenesulphonates leads to a considerable decrease of the reaction rate. Therefore the most reactive aromatic hydrocarbons had to be used and in the present paper mesitylene and pentamethylbenzene were selected since the reaction rate of benzene and toluene is too small for exact measurements. Even using very reactive aromatic hydrocarbons in the case of *m*-nitrobenzyl benzenesulphonate the reaction rate is raised to an acceptable value only if these hydrocarbons are introduced in the reaction in concentrations 10–20 times larger than the ester concentration. In the case of *p*-chlorobenzyl benzenesulphonate and pentamethylbenzene it is possible to take measurements at 1:1 concentrations of the reagents. The use of excess hydrocarbon has the advantage that during the determination no essential change in the reaction medium takes place.

---

[5] C. D. Nenitzescu, S. Titeica and V. Ioan, *Bull. Soc. Chim. Fr.* 1272 (1955).

[6] C. D. Nenitzescu, S. Titeica and V. Ioan, *Bull. Soc. Chim. Fr.* 1279 (1955).

[7] V. Ioan, L. Teodorescu, S. Titeica and C. D. Nenitzescu, *Acad. R.P.R., Studii si Cercetari de Chim.* 7, 345 (1959).

[8] V. Ioan, D. Săndulescu, S. Titeica and C. D. Nenitzescu, cf. following communication, p. 335.

A complication met earlier and in other alkylation reactions of the aromatic nuclei is that the first product (for instance in the case of benzene, diphenylmethane) is further alkylated at a greater rate than the starting hydrocarbon. This of course can change considerably the reaction kinetics. In kinetic measurements made on the reaction between 3,4-dichlorobenzyl chloride and benzene in the presence of aluminium chloride in nitrobenzene, the simplifying hypothesis was made that the mono-, di-, etc. -alkylated product reacts with the same rate as benzene.[9] This drawback does not exist of course in the case of pentamethylbenzene, and in the case of mesitylene is reduced to a minimum by employing an excess of hydrocarbon, as shown above.

The first attempts indicated that besides the sulphonic ester and the catalyst acid, the aromatic hydrocarbon also enters the rate-determining step of the reaction. Indeed the reaction rate is considerably enhanced when in the reaction benzene is replaced by toluene or *m*-xylene.[5]

This fact is general for all electrophilic substitutions of the aromatic nucleus. But most of these reactions were studied in strong ionizing media such as nitromethane and in the presence of a large and constant excess of electrophilic reagent, hence under conditions which cannot be achieved in alkylations. Consequently, there is no simple analogy between the aromatic alkylation and other electrophilic aromatic substitutions or unimolecular and bimolecular substitution reactions of aliphatic compounds.

Reaction mechanism

As shown in a former paper[5] electron withdrawing substituents on the benzyl group decrease the reaction rate, and electron-repelling substituents increase it, in the order $m\text{-NO}_2 < p\text{-Cl} < \text{H} < p\text{-CH}_3$. From Table 1 it is obvious that the large difference in the reaction rate between the m-NO_2 and p-CH_3 substituted benzyl groups (differing by a factor of ca. 6000) is due to a remarkable decrease in the activation energy, compensated partly by an appreciable decrease in the activation entropy.

TABLE 1. RATE CONSTANTS, ACTIVATION ENERGIES AND ACTIVATION ENTROPIES IN THE REACTIONS OF SUBSTITUTED BENZYL BENZENESULPHONATES WITH BENZENE (50° in benzene)

Substituent Y in $YC_6H_4CH_2{\cdot}O{\cdot}O_2SC_6H_5$	$k.10^3$ $l^2.mole^{-2}\,sec^{-1}$	E kcal.mole^{-1}	$\Delta S^{\ddagger}$ cal.mole^{-1} grade^{-1}
m-NO_2	0·016	24·9	−0·78
p-Cl	6·99	14·9	−19·9
H	14·1	6·8	−43·6
p-CH_3	96·7	3·9	−48·7

Two mechanisms of Friedel-Crafts alkylations have been discussed.[10] One is based on a slow, rate-determining ionization of the RX alkylation agent under the action of the catalyst K; an R^+ carbonium ion being formed, which rapidly reacts further with the aromatic hydrocarbon:

$$\left.\begin{array}{l} R{-}X + K \rightleftarrows R^+ + KX^- \\ R^+ + ArH \rightarrow R{-}Ar + H^+ \end{array}\right\} A$$

---

[9] H. C. Brown and M. Grayson, *J. Amer. Chem. Soc.* **75**, 6285 (1953).

[10] For a leading reference see: J. Hine *Physical Organic Chemistry* p. 337. McGraw-Hill, New York (1956); E. S. Gould *Mechanism and Structure in Organic Chemistry* p. 447. Holt and Co., New York (1959).

The second mechanism considers that the action of the catalyst is only to polarize the R—X bond, which thus becomes susceptible to a slow rate-determining nucleophilic atack of the aromatic hydrocarbon:

$$\left.\begin{array}{l} \mathrm{R{-}X + K \rightleftarrows R \ldots\ldots XK} \\ \mathrm{ArH + R \ldots\ldots XK \rightarrow Ar{-}R + HX + K} \end{array}\right\} \mathrm{B}$$

As the bimolecular substitution mechanism requires an inverse influence of the substituents from the benzyl group which was not observed experimentally, mechanism (B) may be neglected.

In fact, the increase in the reaction rate by varying the substituents of the benzyl group in the order $NO_2 < Cl < H < CH_3$ agrees with the destabilizing, and consequently stabilizing effect on the $YC_6H_4CH_2^+$ carbonium ions originating from the substituted benzyl group. This is strong evidence that the formation of such carbonium ions in the rate-determining step play an essential part in the reaction. Another argument is the large negative value of Hammet's constant ρ in the alkylation of benzene ($\rho = -4{\cdot}17$ at 50°).[5]

Even if this conclusion agrees perfectly with the experimental facts, mechanism (A) is, for various reasons, unacceptable in the form presented above. On account of the small dielectric constant and the reduced solvating power of the solvent, it is improbable that R^+ carbonium ions could exist free in solution. In fact, if mechanism (A) is accepted, the reaction rate ought to be proportional to $\sqrt{[RX][K]}$ which, as shown above, does not agree with the experimental facts. On the other hand, if the rate-determining step were only the formation of the R^+ carbonium ion, the reaction rate would be independent of the nature and concentration of the aromatic component, which again is contrary to the observed facts.

Kinetic measurements show that in the rate-determining step both the formation of carbocations and their reaction with the aromatic hydrocarbon intervene. On the other hand, kinetic measurements show that the aromatic hydrocarbon does not enter the reaction rate at the first power as it apparently does in aromatic alkylation catalysed by aluminium chloride.[9]

Any theory on aromatic alkylation must take into account the following facts:

(1) The existence of free R^+ carbonium ions and of the corresponding anions in solvents such as aromatic hydrocarbons and dichloroethane which practically cannot solvate ions is impossible.

(2) A dissociation into ions of the alkylating agent is impossible without the active contribution of a molecular species which has to play the same part for the ion solvation as the solvent molecules in SN1 reactions that take place in protonic solvents.

Considering the above facts, the theory of the alkylation reaction of the aromatic nucleus is based on the following assumptions:

(1) The ionization of the alkylating agent does not go further than the stage of "intimate ion pairs" as Winstein[11] called it. These ion pairs remain enclosed in cages of solvent molecules which are not able to solvate the ions but can take part in the reaction.

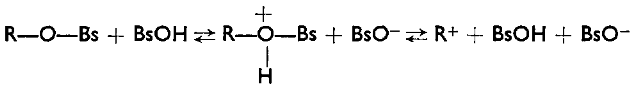
(2) Both the cation and the anion which result from the ionization of the benzenesulphonic ester are each solvated by one molecule of benzenesulphonic acid. This

---

[11] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *J. Amer. Chem. Soc.* **78** 328 (1956).

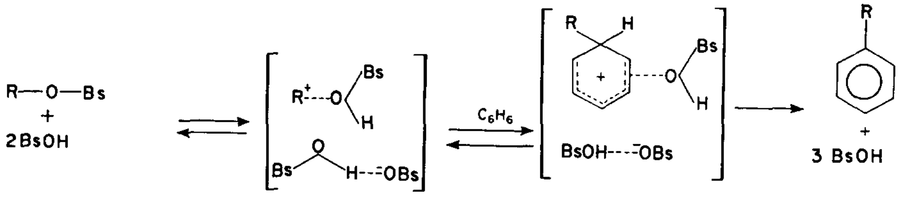
accounts for the fact that *two* molecules of benzenesulphonic acid are involved in the reaction. This also accounts for the great decrease in the activation entropy paralleling the stabilization of the carbonium ions (see Table 1). The two ions and the acid molecules which solvate them form a rigid structural unit where the various components occupy fixed and determined positions.[12] This brings about a considerable decrease in the motion liberty of the various soluted species, thus explaining the decrease in activation entropy.

The ionization reaction of the benzenesulphonic ester under the influence of a proton given by a strong acid can be represented as follows ($R = ArCH_2$; $Bs = C_6H_5SO_2$):



$$R{-}O{-}Bs + BsOH \rightleftarrows R{-}\overset{+}{\underset{H}{O}}{-}Bs + BsO^- \rightleftarrows R^+ + BsOH + BsO^-$$

According to the new conception, this reaction only takes place in the presence of two molecules of benzenesulphonic acid, which are necessary for solvating the BsO^- anion. It is also very probable that the two equilibria mentioned above are established extremely rapidly. Therefore, the oxonium cation is not involved in the reaction kinetics. The stages with kinetic significance may be represented thus: the anion and the cation, each of them solvated by one molecule of benzenesulphonic acid, remain bound as an ion pair in a cage of solvent molecules (represented by square brackets). The cation of this ion pair reacts with a molecule of aromatic hydrocarbon from the solvent cage forming a new ion pair, where the cation is a σ complex of the same type as that proposed by Wheland[13] as intermediates in electrophilic aromatic substitutions. Both ion pairs are imagined as short-lived intermediates but lasting much longer than a molecular collision. The formation of the first intermediate (B) as well as its reaction with the aromatic hydrocarbon for obtaining the second intermediate (C) necessitates activation energy. The collapse of the second intermediate (C) results in the reaction products:



(B) (C)

It is obvious, that in the expression of the total reaction rate, the equilibrium constants of the two reversible reactions must be involved. This allows an interpretation of the reactivity difference found in experiments with various alkylating agents or with various hydrocarbons.

Computation of the kinetic equation

The reaction mechanism proposed can be schematically represented by the following successive reactions, where A is the R—O—Bs ester, X the BsOH acid, H the

---

[12] See a similar conception of E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. Pocker for a reaction of the triphenylmethyl chloride in a solvent of low solvating power: *J. Chem. Soc.* 1265 (1957)

[13] G. W. Wheland, *J. Amer. Chem. Soc.* **64**, 900 (1942).

hydrocarbon and B and C the ion pairs mentioned above:

$$\mathrm{A} + 2\mathrm{X} \underset{-1}{\overset{1}{\rightleftarrows}} \mathrm{B} \tag{I}$$

$$\mathrm{B} + \mathrm{H} \underset{-2}{\overset{2}{\rightleftarrows}} \mathrm{C} \tag{II}$$

$$\mathrm{C} \xrightarrow{3} \text{Reaction products} \tag{III}$$

The equation of the reaction rate was established on the basis that the intermediates B and C are quasistationary.

$$\frac{\mathrm{d}b}{\mathrm{d}t} = k_1ax^2 - k_{-1}b - k_2bh + k_{-2}c = 0$$

$$\frac{\mathrm{d}c}{\mathrm{d}t} = k_2bh - k_{-2}c - k_3c = 0$$

Thus the concentrations corresponding to the stationary state are:

$$b = \frac{k_1(k_{-2} + k_3)ax^2}{(k_{-2} + k_3)(k_{-1} + k_2h) - k_{-2}k_2h}$$

$$c = \frac{k_1k_2ax^2h}{(k_{-2} + k_3)(k_{-1} + k_2h) - k_{-2}k_2h}$$

The total rate equation is therefore:

$$r = -\frac{\mathrm{d}h}{\mathrm{d}t} = k_3c = k_1k_2k_3\frac{ax^2h}{(k_{-2} + k_3)(k_{-1} + k_2h) - k_{-2}k_2h} \tag{1}$$

The form of equation (1) shows that the reaction rate is a hyperbolic function of the concentration h of the aromatic hydrocarbon.

An equation of analogous form concerning the hyperbolic relation between the reaction rate and the concentration of the aromatic hydrocarbon—but not verified experimentally—was established on the basis of a different mechanism in the alkylation of toluene with t-butyl chloride catalysed by hydrofluoric acid.[14]

Noting the initial concentrations of the ester, acid and hydrocarbon with a_0, x_0 and h_0 and knowing that $a + x = a_0 + x_0$ and $h + x = h_0 + x_0$, for the concentrations at time t it results:

$$a = a_0 + x_0 - x = A_0 - x$$

$$h = h_0 + x_0 - x = H_0 - x$$

and equation (1) can be more simply represented thus:

$$r = -\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{ax^2h}{p + sh} = \frac{(A_0 - x)(H_0 - x)x^2}{p + s(H_0 - x)} \tag{2}$$

where $$p = \frac{1}{K_1K_2k_3} + \frac{1}{K_1k_2} \text{ and } s = \frac{1}{k_1}.$$

K_1 and K_2 are the equilibrium constants of equation I and II.

---

[14] J. W. Sprauer and J. H. Simons, *J. Amer. Chem. Soc.* **64**, 648 (1942).

By integration one obtains:

$$t = p\left\{\frac{A_0 + H_0}{(A_0H_0)^2}\ln\frac{x}{x_0} + \frac{1}{A_0H_0}\left(\frac{1}{x_0} - \frac{1}{x}\right) + \frac{1}{A_0^2(H_0 - A_0)}\ln\frac{A_0 - x_0}{A_0 - x} + \frac{1}{H_0^2(A_0 - H_0)}\ln\frac{H_0 - x_0}{H_0 - x}\right\} + s\left\{\frac{1}{A_0^2}\ln\frac{x}{x_0} + \frac{1}{A_0}\left(\frac{1}{x_0} - \frac{1}{x}\right) + \frac{1}{A_0^2}\ln\frac{A_0 - x_0}{A_0 - x}\right\} \tag{3}$$

By examining equation (2) it can be observed that when $sh \ll p$ the rate equation takes the form of an equation of order 4, hence of order 1 in the hydrocarbon. This case corresponds to a very large constant k_1 in the scheme I–III. When $sh \gg p$ the rate equation is of the 3rd order (order zero in the hydrocarbon); the integrated form corresponds to the second term from member 2 of the equation (3) and is the equation used in former papers.[5]

Verification of the kinetic equation

As shown in former papers,[3,5] the alkylation of aromatic hydrocarbons with benzyl benzenesulphonates presents experimental advantages for the establishment of the reaction kinetics, such as the temperature range, dilute solutions, homogenous media and lack of secondary reactions. In former papers only the reaction order in the alkylation agent and the acid catalyst were established by employing hydrocarbon media. In the present kinetic measurements dichloroethane was used since it is a good solvent for all components of the system. By varying the concentration of the aromatic hydrocarbon the kinetic order in the hydrocarbon was found.

Alkylation of mesitylene and pentamethylbenzene with p*-chlorobenzyl benzenesulphonate*

In Table 2 and 3 the initial concentrations of *p*-chlorobenzyl benzenesulphonate, benzenesulphonic acid, mesitylene, and pentamethylbenzene are given respectively. The ester and acid concentrations were maintained practically constant in the same series of determinations in order to obtain comparable values for k_3 without needing corrections for the association acid ester.[8] The hydrocarbon concentration was varied over a wide range, taking generally an excess over the stoichiometric value in order to avoid polyalkylation reactions.

TABLE 2. KINETIC DATA OF REACTION BETWEEN *p*-CHLOROBENZYL BENZENESULPHONATE AND MESITYLENE IN DICHLOROETHANE AT 50°

No.	a_0 mole/l	x_0 mole/l	h_0 mole/l	k_3 l^2.mole^{-2} min^{-1}	h_0/k_3 l^{-3}.mole^3 min
1	0·020	0·010	0·25	2·21 ± 0·01	0·113
2	0·020	0·010	0·50	3·74 ± 0·01	0·134
3	0·019	0·012	1·00	6·26 ± 0·01	0·160

The reactivity and the self-alkylation of *p*-chlorobenzyl benzenesulphonate was controlled thus: a solution of 0·56 mole/l ester and 0·01 mole/l benzenesulphonic acid in dichloroethane without hydrocarbon at 50° shows no increase of acidity after 35 hr, which is longer than the time of the slowest experiments with mesitylene.

Table 3. Kinetic data of reaction between p-chlorobenzyl benzenesulphonate and pentamethylbenzene in dichloroethane at 50°

No.	a_0 mole/l	x_0 mole/l	h_0 mole/l	k_3 $l^2.\text{mole}^{-2}\,\text{min}^{-1}$	h_0/k_3 $l^{-3}.\text{mole}^3\,\text{min}$
1	0·019	0·011	0·0194	1·36 ± 0·01	0·014
2	0·019	0·011	0·0490	3·25 ± 0·01	0·015
3	0·019	0·011	0·0990	6·14 ± 0·01	0·016
4	0·019	0·011	0·1490	8·84 ± 0·01	0·017

The k_3 rate constants from these Tables were computed according to the rate equation of 3rd order which was also used in the former paper:[5]

$$k_3 = \frac{1}{t}\left[\frac{1}{A_0^2}\ln\frac{x}{x_0} + \frac{1}{A_0}\left(\frac{1}{x_0} - \frac{1}{x}\right) + \frac{1}{A_0^2}\ln\frac{A_0 - x_0}{A_0 - x}\right] \tag{4}$$

The k_3 values are the average of constants computed at various intervals until a conversion of p-chlorobenzyl benzenesulphonate of 60–70% was reached.

The variation of constant k_3 with the initial concentration of the hydrocarbon is represented in Fig. 1 for mesitylene and in Fig. 2 for pentamethylbenzene.

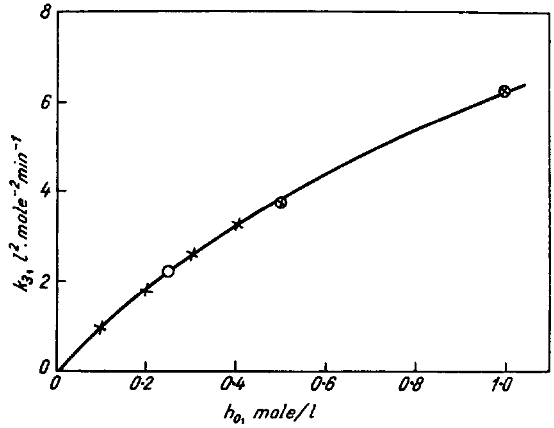


Fig. 1. Variation of the rate constant k_3 with the hydrocarbon concentration in the reaction of p-chlorobenzyl benzenesulphonate with mesitylene in dichloroethane at 50°. (○ experimental values; + computed values)

From equation (2) it results that if the aromatic hydrocarbon is in sufficient excess in comparison with other components its concentration can be considered practically constant during an experiment and equation (2) becomes:

$$r = k_{3(\text{apparent})}\,(A_0 - x)x^2 \tag{5}$$

where k_3 (apparent) computed with equation (4) and given in Table 2 and 3 is:

$$k_{3(\text{apparent})} = \frac{h_0}{p + sh_0} \qquad (\text{for } h \approx h_0) \tag{6}$$

The equation (6) shows that the relation between k_3 (apparent) and h_0 is a hyperbolic function. In this case h_0/k_3 must be a linear function of the hydrocarbon concentration. The graphic representation of the ratio h_0/k_3 versus h_0 is given in Fig. 3.

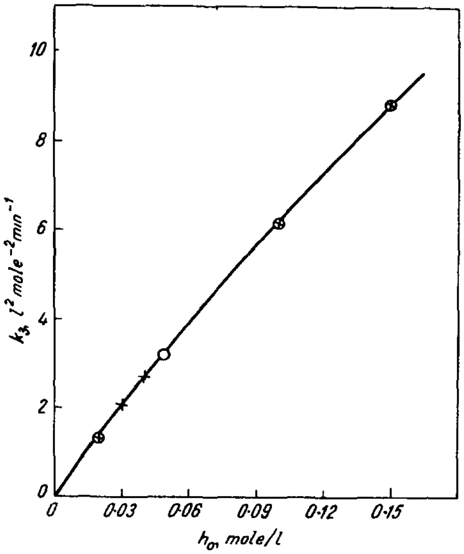


FIG 2. Variation of the rate constant k_3 with the hydrocarbon concentration in the reaction of *p*-chlorobenzyl benzenesulphonate with pentamethylbenzene in dichloroethane at 50°.
(○ experimental values; + computed values)

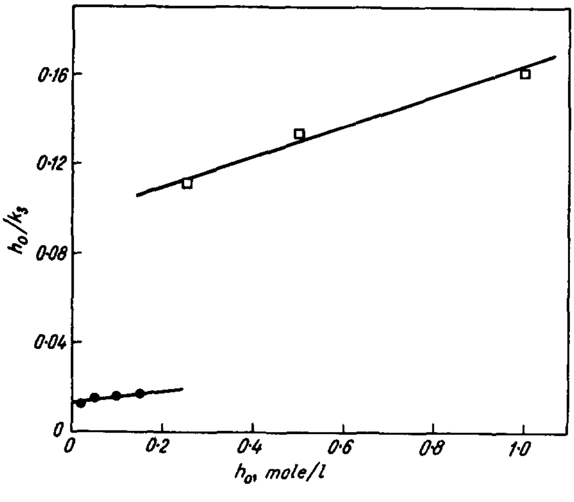


FIG. 3. Variation of the ratio h_0/k_3 versus h_0 for the reactions of *p*-chlorobenzyl benzenesulphonate with mesitylene (□) and pentamethylbenzene (●) in dichloroethane at 50°.

The values of constants p and s were determined by the means method admitting that the ratio h_0/k_3 is linear depending on h_0. The values obtained were for mesitylene, $p = 0{\cdot}1$ and $s = 0{\cdot}06$; for pentamethylbenzene, $p = 0{\cdot}014$ and $s = 0{\cdot}019$; these values refer to the units of concentration and time from Tables 2 and 3. These p and s values were introduced into equation (6) and the values computed for k_3 are also represented in Figs. 1 and 2.

The agreement of the experimental data with the established equation (6) was verified by the Gauss criterion in comparison with the straight line which passes through the origin, therefore corresponding to the case when the rate equation would be of order 1 in the hydrocarbon. The following results were obtained:

Gauss criterion

	Mesitylene	Pentamethylbenzene
Case 1: order 1 in hydrocarbon	0·27	0·05
Case 2: rate equation (6) hyperbolic function of hydrocarbon concentration	0·05	0·0046

From the above data the minimum value of the Gauss criterion shows the validity of equation (6) for the representation of the experimental data.

In the case of experiments with pentamethylbenzene the equation (6) was also verified by the method of initial rates; it agrees well with the experimental data.

Alkylation of pentamethylbenzene with m-*nitrobenzyl benzenesulphonate*

Table 4 contains kinetic data of the alkylation of pentamethylbenzene with *m*-nitrobenzyl benzenesulphonate at 70° and Table 5 at 80°.

Table 4. Kinetic data of the reaction between m-nitrobenzyl benzenesulphonate with pentamethylbenzene in dichloroethane at 70°

No.	a_0 mole/1	x_0 mole/1	h_0 mole/1	k_3 1^2.mole^{-2} min^{-1}	h_0/k_3 1^{-3}.mole^3 min
1	0·0295	0·0306	0·2994	0·158 ± 0·003	1·89
2	0·0296	0·0303	0·3746	0·199 ± 0·003	1·88
3	0·0296	0·0305	0·4496	0·231 ± 0·003	1·94
4	0·0298	0·0315	0·5552	0·275 ± 0·003	2·02

Table 5. Kinetic data of the reaction between m-nitrobenzyl benzenesulphonate with pentamethylbenzene in dichloroethane at 80°

No.	a_0 mole/1	x_0 mole/1	h_0 mole/1	k_3 1^2.mole^{-2} min^{-1}	h_0/k_3 1^{-3}.mole^3 min
1	0·050	0·046	0·100	0·071 ± 0·001	1·40
2	0·050	0·051	0·125	0·088 ± 0·001	1·43
3	0·050	0·051	0·150	0·106 ± 0·001	1·41
4	0·050	0·052	0·175	0·124 ± 0·001	1·41
5	0·050	0·051	0·200	0·143 ± 0·001	1·41

The data from these Tables were computed similarly to those from the experiments with *p*-chlorobenzyl benzenesulphonate given above. The diagram from Fig. 4 for the reaction at 70° was obtained by the same linearization procedure.

A hyperbolic variation of the constant k_3 with h_0 and a linear variation of the h_0/k_3 ratio with h_0 can be observed. The p and s constants are 1·716 and 0·525 respectively.

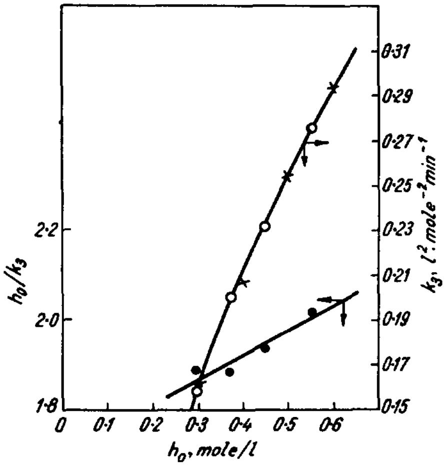


FIG. 4. Graphic verification of equation (6) for the reaction of *m*-nitrobenzyl benzenesulphonate with pentamethylbenzene in dichloroethane at 70°. (○ variation of k_3 with h_0; ● variation of h_0/k_3 with h_0; + computed values).

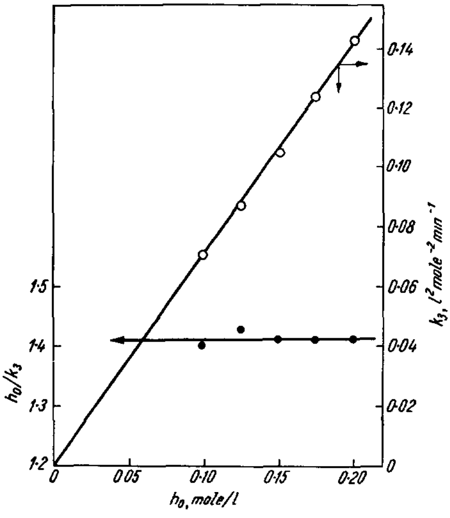


FIG. 5. Graphic verification of equation (6) for the reaction of *m*-nitrobenzyl benzenesulphonate with pentamethylbenzene in dichloroethane at 80°. (○ variation of k_3 with h_0; ● variation of h_0/k_3 with h_0).

Applying the Gauss criterion in comparison with the case of order 1 in the hydrocarbon leads to the following results: the mean square error of order 1 is 4×10^{-5} and for the case of the equation (6) is 2×10^{-6}. The validity of equation (6) in comparison with an equation of order 1 in the hydrocarbon can therefore also be observed in this case.

The data from Table 5 are represented in the diagram from Fig. 5 which shows the linear variation of the constant k_3 with h_0 with a mean square error of 25×10^{-8}. In this case the reaction is practically of order 1 in the hydrocarbon, which shows that the value of the s constant from equation (6) is very much decreased (it is practically zero).

This decrease of s corresponds, in the scheme I–III, to a large increase of the constant k_1 with the temperature because $s = 1/k_1$.

As was shown, the general kinetic equation of the alkylation reaction established in the present paper can account for a reaction order equal to one in the hydrocarbon, as was observed in the Friedel-Crafts reactions studied by Brown and Grayson,[9] because in the case when $sh \ll p$ the term which contains the hydrocarbon concentration vanishes from the denominator of the equation rate. This condition is fulfilled in the case of certain alkylation agents, as those used by Brown, or above certain working temperatures, because the increase of constant k_1 with the temperature is much greater than that of other constants.

The equation established on the basis of the mechanism proposed above is similar to the equation established by Brown on the basis of a different mechanism which was not however verified for establishing the hyperbolic variation of the reaction rate with the hydrocarbon concentration; only the limiting case presented above was used.

Concerning the aromatic alkylation with benzyl halides catalysed by benzenesulphonic acid,[1,6,7] recent experiments similar to those described above, aiming at establishing the order of the hydrocarbon, show that the intervention of the hydrocarbon in the equation rate cannot be explained only by applying the theory in the form exposed above; this implies a slightly different chemical reaction, as will be shown in a future communication.

EXPERIMENTAL

Starting materials

p-*Chlorobenzyl and* m-*nitrobenzyl benzenesulphonate* were prepared according to the methods proposed in former paper.[5]

Mesitylene purified by sulphonation and hydrolysis of the mesitylenesulphonic acid,[15] $n_D^{25} = 1{\cdot}49684$.

Pentamethylbenzene prepared by methylation of xylene with methyl chloride in the presence of aluminium chloride;[16] m.p. 51·5°.

Pure commercial dichloroethane dried on P_2O_5 and distilled, $n_D^{20} = 1{\cdot}44471$.

The solution of anhydrous benzenesulphonic acid in dichloroethane was prepared by dissolving distilled benzenesulphonic acid[17] in dichloroethane and by diluting these solutions to working concentrations.

Kinetic determinations

A Hoeppler thermostat with ±0·05° precision was used. The reaction was effected in a 750 ml flask provided with a sealed-in cooler large enough to allow 10 ml samples to be pipetted off.

The starting solution was prepared by weighing the benzylic ester and the hydrocarbon; a known volume of concentrated solution of benzenesulphonic acid in dichloroethane was added and then made up to 500 ml with dichloroethane.

In order to follow the reaction in time, the benzenesulphonic acid in the 10 ml sample was titrated. The quantity of acid formed, corresponding to the reacted benzenesulphonated ester, was computed from the difference between the acidity at time t and the starting acidity. Titrations were made with 0·05N KOH solution using a mixed indicator neutral red–methylene blue.[5]

---

[15] R. Adams and R. W. Hufferd *Organic Syntheses* coll. vol. I; p. 341. John Wiley, New York, (1947).

[16] H. Clément, *Ann. Chim. Fr.* [13–14], 243 (1940).

[17] H. V. Kehiaian and C. D. Nenitzescu, *Chem. Ber.* **90**, 685 (1957).