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MECHANISM OF AROMATIC ALKYLATION—VI

INFLUENCE OF THE ASSOCIATION OF REACTANTS ON THE REACTION KINETICS[1]

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

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Abstract—Kinetic measurements in the alkylation of benzene with benzyl benzenesulphonate catalysed by benzenesulphonic acid were effected, by varying on a wide range the concentration ratio of ester and acid. The apparent rate constants, computed on the basis of the kinetic equation formerly deduced, decrease with the increase of the starting ester concentration. They were recalculated on the basis of a corrected equation in which the concentration of the acid unassociated with the ester (deduced from the acid-ester association equilibrium) took the place of the analytical concentration of benzenesulphonic acid. The real rate constant and the constant of the association equilibrium were calculated. The value of the latter constant thus found coincides with the association constant ester-acid determined by ebulioscopy in a similar case.

THE study of the alkylation of aromatic hydrocarbons with substituted benzyl benzenesulphonates in an inert solvent led to a general kinetic equation, according to which the reaction rate is a function of 1st order in the concentration of the benzenesulphonic ester, of 2nd order in the concentration of benzenesulphonic acid and a hyperbolic function in the concentration of the aromatic hydrocarbon.[1,2] The equation agrees fairly well with the experimental data.

The proposed reaction mechanism[1] is based on the hypothesis that the ionization of the benzenesulphonic ester is possible because the anion and the cation are each solvated by one molecule of benzenesulphonic acid forming a pair of solvated ions in a cage of unpolar solvent molecules.

Previous papers from this laboratory[3,4] showed by ebuliometric measurements that in benzene solution the benzenesulphonic acid associates with itself and with benzenesulphonic esters. The existence of these association phenomena under the conditions in which the reactions of aromatic alkylation take place, gives rise to the following problems: (1) whether the association influences the mechanism of aromatic alkylation and (2) whether the variations of rate constants of alkylation reactions experimentally found under various working conditions can be quantitatively interpreted by considering the association process.

In order to elucidate these questions measurements of reaction rate were made in the alkylation of benzene with benzyl benzenesulphonate, catalysed by benzenesulphonic acid in excess benzene as solvent. In these measurements, unlike previous ones[1,2] the ratio between the concentration of ester and of acid catalyst was varied on a wide range.

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[1] Part V: V. Ioan, D. Săndulescu, S. Titeica and C. D. Nenitzescu, preceding paper p. 323.

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

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

[4] H. V. Kehiaian, *Acad. R.P.R. Studii si Cercetari de Chim.* **7**, 603 (1959).

In Table 1 the initial concentrations of benzyl benzenesulphonate (a_0) and of benzenesulphonic acid (x_0) (varying in the ratio 1·5–62) for six experiments at 50° are given. The rate constants k' were calculated according to the equation of third order used in former papers:

$$\frac{dx}{dt} = k'(a_0 + x_0 - x)x^2 = k'ax^2 \tag{1}$$

(x is the concentration of benzenesulphonic acid at time t).

By integrating the equation (1) one obtains:

$$k' = \frac{1}{t}\left[\frac{1}{(a_0 + x_0)^2}\ln\frac{a_0 x}{(a_0 + x_0 - x)x_0} + \frac{1}{a_0 + x_0}\left(\frac{1}{x_0} - \frac{1}{x}\right)\right] \tag{2}$$

This equation can also be deduced from the general equation (3) in the preceding paper[1] for the case when the initial concentration of the hydrocarbon h_0 is very high (the hydrocarbon used as solvent) and consequently practically constant during the reaction. By introducing the experimental values in equation (2) the rate constants k' from Table 1 were obtained.

TABLE 1. KINETIC DATA FOR THE ALKYLATION OF BENZENE WITH BENZYL BENZENESULPHONATE AT 50°

No.	a_0 mole/l	x_0 mole/l	a_0/x_0	k'* l^2.mole^{-2} min^{-1}	$\frac{1}{\sqrt{k'}}$
1	0·00578	0·00397	1·5	11·85	0·291
2	0·0174	0·00308	5·6	9·27	0·328
3	0·0371	0·00302	12	7·62	0·362
4	0·0594	0·00206	29	6·27	0·399
5	0·0997	0·00215	46	4·07	0·496
6	0·1347	0·00215	62	3·35	0·546

* Mean values

From the data given in Table 1 and plotted in Fig. 1, a decrease in the rate constants with an increase of the initial ester concentration is observed.

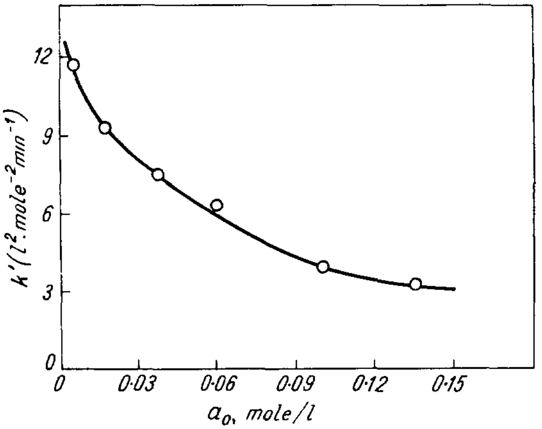

FIG. 1. Variation of the rate constant k' with the initial concentrations of benzyl benzenesulphonate (a_0).

Calculation of rate constant

The variation of the rate constants k' may be attributed either to a modification of the general kinetic equation, or to the association acid-ester and acid-acid, or to both these causes.

First the association phenomena established previously by thermodynamic methods were considered. For calculating the k' constants in equation (2) the analytical concentrations of ester and acid were introduced. The ester concentration at the moment t is correctly given by the expression $a_0 + x_0 - x$, because this value results from a stoichiometric ratio. Thus it is plausible that the real concentration of the benzenesulphonic acid in uncombined form, when it behaves as a catalyst, is not equal to the value x analytically determined but has a smaller value since part of the acid is associated with the ester. As the sulphonic ester is more basic than the benzenesulphonic acid, it is plausible that the fraction of acid which is associated with the ester interferes only to a negligible extent or not at all in the catalysis. Thus in the rate equation, instead of the analytical concentration x, the value $x - \eta$ must be introduced, where η is the number of moles per litre of acid associated with the ester. The rate equation (1) thus corrected has the following form:

$$\frac{dx}{dt} = k(a_0 + x_0 - x)(x - \eta)^2 = ka(x - \eta)^2 \tag{3}$$

Between the ester (A) and the acid (X) several association types are possible. Because of the excess of ester corresponding to the experimental conditions chosen the association may be represented by a simple reaction as follows:

$$\underset{\text{associated form}}{X + A \rightleftharpoons X{\cdot}A} \tag{I}$$

The thermodynamic equilibrium equation may be applied to the association reaction (I):

$$K = \frac{\eta}{(x - \eta)(a - \eta)} \cong \frac{\eta}{(x - \eta)a_0} \tag{4}$$

where K is the equilibrium constant; this approximation is justified by the excess of ester, $a_0 \gg x > \eta$ for the initial period of a reaction. Thus the concentration of the associated form η will be the following:

$$\eta = \frac{xa_0K}{1 + Ka_0} \tag{5}$$

which, introduced in the rate equation (3), leads to:

$$\frac{dx}{dt} = k\left(1 - \frac{Ka_0}{1 + Ka_0}\right)^2 ax^2 = k'ax^2 \tag{6}$$

The corrected rate equation (6) shows that the value of constant k' computed by simple application of equation (1) corresponds to an apparent rate constant which is a function of the ester concentration. (For the initial period of the reaction the ester concentration is considered to be equal to a_0.)

$$k' = \frac{k}{(1 + Ka_0)^2} \tag{7}$$

In equations (6) and (7) k is the corrected rate constant for the experimental concentration range; its value must be close to the real value.

The equation (7) may be written in the form:

$$\frac{1}{\sqrt{k'}} = \frac{1}{\sqrt{k}} + \frac{Ka_0}{\sqrt{k}} \tag{8}$$

Thus equation (7), corresponding to the association scheme (I), can be verified (according to equation 8) if $1/\sqrt{k'}$ has a linear variation versus a_0. The diagram from Fig. 2 shows that the equation (7) is verified in the whole concentration range. In this verification, average values of the k' constant during one experiment were used; no significant differences were obtained by using the initial values of the constant k' and in many cases the extrapolation of k' at $t = 0$ was not necessary, since for the first data of an experiment k' is practically constant.

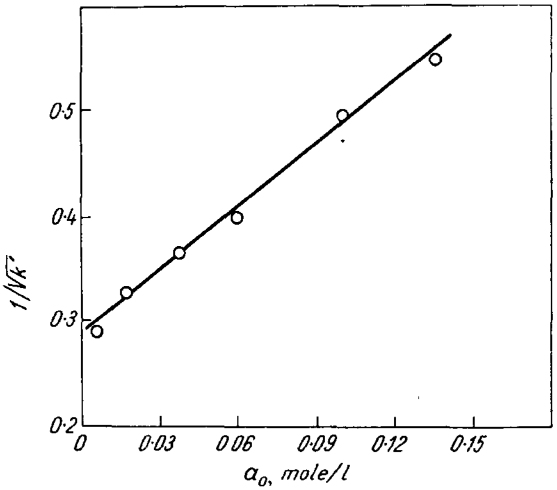

FIG. 2. Variation of $1/\sqrt{k'}$ versus the initial concentrations of benzyl benzenesulphonate (a_0).

By applying equation (8) the value $K = 6{\cdot}9 \pm 0{\cdot}1$ is obtained for the constant of the association equilibrium (the concentrations are given in mole/l), and the value $k = 12{\cdot}2 \pm 0{\cdot}3\ \mathrm{l}^2.\ \mathrm{mole}^{-2}\ \mathrm{min}^{-1}$ for the rate constant.

The constant K computed thus indirectly from kinetic data has a value close to that determined by ebuliometric methods for the association of benzenesulphonic acid with methyl benzenesulphonate in benzene at 80°, for which a value of 9·7–9·3 was found.[4] (The direct determination of the association constant of benzenesulphonic acid with benzyl benzenesulphonate cannot be effected because of the instability of the latter ester.)

The values of the rate constant k' interpolated for the concentration range 0·01–0·02 mole/l ester agree with the data obtained in the former paper[2] in which we used this concentration range.

The rate constants k' computed for various values t during the same experience generally present a small increase, especially above 30% conversions of benzyl benzenesulphonate and a more pronounced increase for greater a_0 values, as shown in

Table 2 which comprises the values corresponding to experiments 2, 4 and 5. This increase can be interpreted by the decrease of the ester concentration which according to the equilibrium equation (4) leads to an increase of the free acid catalyst.

TABLE 2. RATE CONSTANTS k' COMPUTED FROM EQUATION (2)

$a_0 = 0·0174$ mole/l			$a_0 = 0·0594$ mole/l			$a_0 = 0·0997$ mole/l		
$x_0 = 0·00308$ mole/l			$x_0 = 0·00206$ mole/l			$x_0 = 0·00215$ mole/l		
t min.	x mole/l	k' $l^2.mole^{-2} min^{-1}$	t min.	x mole/l	k' $l^2.mole^{-2} min^{-1}$	t min.	x mole/l	k' $l^2.mole^{-2} min^{-1}$
550	0·00418	9·23	675	0·00415	6·16	765	0·00557	3·80
560	0·00423	9·39	815	0·00519	6·14	840	0·00675	3·88
815	0·00501	9·29	915	0·00627	6·12	900	0·00813	3·89
1110	0·00622	9·18	1015	0·00792	6·12	960	0·0102	3·93
1295	0·00728	9·19	1075	0·00952	6·15	1020	0·0141	3·99
1445	0·00838	9·23	1135	0·0119	6·18	1050	0·0176	4·03
1535	0·00908	9·20	1175	0·0142	6·22	1070	0·0213	4·07
1655	0·0103	9·26	1195	0·0160	6·26	1090	0·0269	4·11
1715	0·0111	9·34	1225	0·0191	6·29	1105	0·0337	4·15
1815	0·0121	9·29	1255	0·0238	6·35	1115	0·0410	4·19
1955	0·0137	9·30	1285	0·0309	6·42	1125	0·0514	4·23
2090	0·0153	9·30	1315	0·0413	6·51	1135	0·0658	4·28
2210	0·0167	9·37	1345	0·0523	6·63	1146	0·0842	4·34
	mean value	9·27		mean value	6·27		mean value	4·07

Equation (7) results in:

$$\frac{dk'}{k'} = -\frac{2K da}{1 + Ka} \tag{9}$$

Equation (9) shows qualitatively the sign of the variation of k' with the decrease of the ester concentration a: $da < 0$ hence $dk' > 0$, as the experimental data also show. On the other hand on the basis of equation (9) there is a fair agreement between the relative variations $\Delta k'/k'$ experimentally observed and those computed by substituting the infinitesimal differences with finite differences for the first 4–5 points of an experiment. This verification confirms that the continuous (but small) increase of constant k' during an experiment can be generally attributed to the increase of the free acid concentration corresponding to the amount of reacted ester.

A second association scheme:

$$2X + A \rightleftarrows X_2 \cdot A \quad \text{or} \quad X_2 + A \rightleftarrows X_2 \cdot A \tag{II}$$

cannot be taken in the discussion because a calculation similar to that shown above does not explain the variation of k' depending on a_0.

Discussion of the results

As it was shown, the kinetic data obtained with different concentrations of acid and ester can be satisfactorily interpreted on the basis of the association of benzyl benzenesulphonate with benzenesulphonic acid. The effect of the ester concentration is to bind a part of the acid catalyst under the form of practically inactive associates.

Should the associates ester-acid have a catalytic role, the equation of the reaction rate would be following:

$$\frac{dx}{dt} = k'[A][X]^2 + k''[A][X{\cdot}A]^n \tag{10}$$

If the second term from the equation (10) had a kinetic contribution, the effect would be observed towards high values of the ratio a_0/x_0. On the contrary, the experimental data show that $k'' \ll k'$ or $k'' = 0$.

Because the ester has a larger concentration than the acid it is not necessary to discuss the association acid-acid. The molecules of benzenesulphonic acid are involved in the catalysis either as distinct or as associated molecules, and owing to the rapid association equilibrium, it is impossible to specify on the basis of kinetical data which are the active species.

The recalculation of the rate constant on the basis of the above arguments shows that the integrated form (3) of the rate equation from the preceding paper[1] can be generally applied on condition that the value x must correspond to the concentration of the acid unassociated with the ester. The results confirm that the reaction mechanism is not influenced by the association of the reagents.

EXPERIMENTAL

Starting materials

Tiophene-free benzene, dried over sodium m.p. 5·1°, $n_D^{25} = 1{\cdot}49790$.

The solution of benzenesulphonic acid in benzene was prepared by dissolving the distilled benzenesulphonic acid[3] in benzene and by diluting these solutions to the desired concentrations.

Benzyl benzenesulphonate was prepared according to Földi[5] and dissolved in benzene. The ester concentration was determined by hydrolysis.[3]

Kinetic determinations

A Hoeppler thermostat at a temp. of 50 ± 0·05° was used. The reaction took place in a 750 ml flask with sealed-in cooler through which samples could be withdrawn by means of a 10-ml pipet.

The initial solution was prepared by mixing adequate volumes of concentrated solutions of benzenesulphonic acid and benzyl benzenesulphonate and by diluting at 500 ml with benzene. The initial concentrations of the reagents were determined by titrating the acidity and by hydrolysis of the ester.

The reaction was followed in time by the titration of the total benzenesulphonic acid in 10 ml samples, as shown in the preceding paper.[1]

[5] Z. Földi, *Ber. Dtsch. Chem. Ges.* **60**, 656 (1927).