

## DEHALOGENATION OF CHLOROBENZENES WITH SODIUM DIHYDRIDOBIS(2-METHOXYETHOXO)ALUMINATE

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The dehalogenation of a series of 9 mono- to pentachlorinated benzenes with the title hydride in toluene has been found to be first order in the substrate and half order in the hydride. The reactivities of the chlorobenzenes, expressed by rate constants for the first-step dehalogenation, increased with increasing number of chlorine atoms over three orders of magnitude. The rate data revealed the unexpected acceleration of benzene formation during exhaustive dehalogenation of the higher chlorinated benzenes. For comparison, dehalogenation of several isomeric dibromobenzenes and bromochlorobenzenes with the same hydride and the product distribution for the dehalogenation of some chlorobenzenes with  $\text{LiAlH}_4$  are also reported.

In recent years, a renewed interest in dehalogenation of chlorinated aromatic hydrocarbons with metal hydrides has appeared especially in connection with the study of destruction of toxic polychlorinated pollutants (for recent review see e.g. ref.<sup>1</sup>). The hydrides claimed effective for this purpose included  $\text{NaH}$  (refs<sup>2,3</sup>),  $\text{CaH}_2$  (ref.<sup>3</sup>),  $\text{NaBH}_4$  (ref.<sup>4</sup>),  $\text{NaBH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  (ref.<sup>5</sup>),  $\text{LiAlH}_4$  (refs<sup>3,6,7</sup>), and lately also  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  (refs<sup>8,9</sup>). By contrast, metal hydrides in general turned out to be poor agents for dehalogenation of nonactivated aryl chlorides such as chlorobenzene, chlorotoluenes or chloronaphthalenes (for  $\text{LiAlH}_4$  see refs<sup>10,11</sup>,  $\text{NaAlH}_4$  cf. ref.<sup>12</sup>, and for  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  see refs<sup>13,14</sup>). However, except  $\text{LiAlH}_4$  (ref.<sup>11</sup>), a sufficiently broad series of aryl chlorides has not been studied in other cases to express these differences in terms of structure–reactivity relationships. In the course of our study of the detoxification of PCB-contaminated nonpolar liquids based on nucleophilic substitutions<sup>9,15</sup>, we have examined for comparison also similar reactions of benzene analogues.

In the present work we report on the dehalogenation of a series of mono- to pentachlorinated benzenes with sodium dihydridobis(2-methoxyethoxo)aluminate (SDMA). Kinetic study of the reaction was made with the final aim to relate the rate data obtained to structure effects.

## EXPERIMENTAL

### Chemicals

Toluene (p.a., Lachema Brno) was used as obtained. Tetrahydrofuran (purum, VEB Laborchemie Apolda) was dried over sodium aluminium hydride and redistilled. SDMA (Synhydrid, Synthesia Kolín, 70% solution of  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  in toluene) was used after volumetric determination of the hydride concentration prior to each series of kinetic measurements.

The following chlorobenzenes were commercial samples: chlorobenzene (p.a., Lachema Brno), 1,4-dichloro- and 1,2-dichlorobenzene (purum, Lachema Brno), 1,3-dichlorobenzene, 1,2,3-trichloro-, 1,2,4,5-tetrachloro- and pentachlorobenzene (all purum, Fluka), 2- and 4-bromochlorobenzene, 1,3- and 1,4-dibromobenzene (purum, Koch-Light Lab.). 1,2,3,5-Tetrachlorobenzene was prepared by the Sandmayer reaction<sup>16</sup> from 2,4,6-trichloroaniline, by diazotation in hydrochloric acid solution and by decomposition of the diazonium salt by  $\text{CuCl}$  in hydrochloric acid at 60 °C. The crude product was extracted to diethyl ether and the tetrachloro derivative was obtained by crystallization from the ether layer after partial removal of the solvent by evaporation. Because of its low purity, the product was used only to GC-MS identification of the tetrachlorobenzene formed during dehalogenation of pentachlorobenzene. 1,2,4-Trichlorobenzene was obtained analogously starting from 2,4-dichloroaniline (purum, Merck). The obtained liquid was purified by distillation under reduced pressure (98% purity by GLC analysis).

### Dehalogenation with SDMA in Excess

To a thermostated reaction vessel provided with a thermometer and a reflux condenser and containing dry toluene (13 ml), the known volume of SDMA solution (60% hydride concentration) was added, and the mixture was heated to reaction temperature. Then, preheated, ca 0.4 M solution of chlorobenzene (2 ml, 7 – 8 mmol) in toluene was added in one portion, and the magnetically stirred reaction mixture was kept at the required temperature while withdrawing samples (0.5 ml) at fixed time intervals. In each measurement the hydride was in threefold molar excess with respect to the chlorine of the chlorobenzene used. In the samples of the reaction mixture, the excess hydride was immediately decomposed by shaking with 2 M aqueous hydrochloric acid (5 ml), and after separation, a part of the toluene layer was used directly to GLC analysis or it was dissolved in cyclohexane when the distribution of dehalogenation products was determined by GC-MS method.

### Equimolar Dehalogenation of Pentachlorobenzene with SDMA

The reaction of pentachlorobenzene (8.4 mmol) and SDMA (8.1 mmol) dissolved in toluene (30 ml) was carried out at 70 °C in the reaction vessel described above. The first sample analyzed was that of the blank mixture (without pentachlorobenzene) and then the samples of the reaction mixture were withdrawn (in initial phases 2 ml, later 3 ml each) at 10, 30, 120, and 240 min with the aid of the preheated and argon-filled hypodermic syringe. The samples were immediately poured into 0.2 M benzene solution of iodine and retitrated by 0.05 M aqueous sodium thiosulfate, as reported<sup>17</sup>. Along with the samples for the iodometric determination of SDMA, also those for GLC analysis (see below) were taken from the reaction mixture at the same time intervals.

### Dehalogenation with $\text{LiAlH}_4$ in Excess

To the apparatus described (vide supra), dry tetrahydrofuran (THF, 15 ml) was added, along with  $\text{LiAlH}_4$  in the amount which ensured threefold molar excess of the hydride hydrogen with respect to the chlorine of the chlorobenzene studied. The suspension was heated to 63 °C with stirring, and the

reaction was started by adding preheated solution of chlorobenzene (2 ml, 7 – 8 mmol) in THF. The samples of the reaction mixture (ca 0.5 ml) were withdrawn at fixed time intervals, the excess hydride was immediately decomposed by shaking with diluted aqueous hydrochloric acid (1 : 1 v/v, 5 ml), and the mixture was extracted by toluene (0.5 ml). After distinct separation of both phases, the sample of the toluene layer was subjected to GLC analysis.

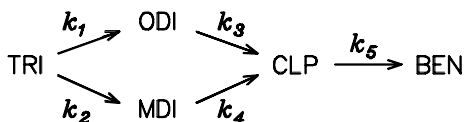
#### Analysis of Dehalogenation Mixtures

*GC-MS Method.* The analysis was made on a Varian 3500 capillary gas chromatograph coupled with a Finnigan MAT ITD 800 ion trap mass detector (EI 70 eV) and equipped with LEO PC 386 SX computer for data processing. A J & W quartz column (30 m × 25 mm × 0.25 μm, DB-5 SE 54 silicone elastomer phase) was used for a high resolution separation (helium as the carrier gas). The initial column temperature was 40 °C (5 min hold), followed by temperature increase by 10 °C/min to 70 °C and then by 20 °C/min to the final 250 °C. The splitless injection port and transfer line were held at 225 and 250 °C, respectively. The ITD full-scale acquisition range was from 33 to 350 a.m.u., with a peak threshold of 1 count for full scan. The selected ions monitored were 112, 146, 180 and 182, 214 and 216, 248 and 250 for mono- to pentachlorobenzene, respectively. The data acquisition was started at 5 min. The method was used for the analysis of the course of pentachlorobenzene dehalogenation. For this purpose, the calibration was made with the use of test mixtures (see Table I for calibration parameters).

*GLC Method.* The course of dechlorination of the lower chlorinated benzenes (chlorobenzene, dichlorobenzenes, and trichlorobenzenes) was followed by GLC (Hewlett–Packard 5890 chromatograph equipped with a 25 m glass capillary column (0.25 mm i.d.) covered with OV-101 silicone phase, FID detector, temperature range 30 – 200 °C). Because of the sensitivity of the response of the FID detector to the number of chlorine atoms in the compounds to be detected, the instrument was calibrated for the range of the conversions of the chloro compounds followed in kinetic experiments, using the method of internal standard (for calibration parameters see Table I). The analysis made it possible to determine also the amount of benzene formed as the final product of the dehalogenations.

#### Treatment of Experimental Data

Experimental data on concentration changes of individual components of the reaction mixture (the starting substrate and dehalogenation products) in dependence on time were fitted according to the proposed reaction scheme involving a set of parallel and consecutive dehalogenations. The fit of experimental data was estimated on the basis of average standard deviations for each time–concentration dependence. The set of differential first-order kinetic equations was written and simultaneously solved numerically according to the Runge–Kutta method. The optimization of the equation parameters with respect to experimental data was made by a modified Marquardt method<sup>18</sup>. The procedure yielded a set of rate constants for individual reaction steps. Thus, for example, the dechlorination of 1,2,3-trichlorobenzene was described by the following reactions (Scheme 1):



SCHEME 1

TRI stands for 1,2,3-trichlorobenzene, ODI for 1,2-dichlorobenzene, MDI for 1,3-dichlorobenzene, CLP for chlorobenzene and BEN for benzene. The corresponding differential equations had the following form:

$$d[\text{TRI}]/dt = -k_1[\text{TRI}] - k_2[\text{TRI}] \quad (1)$$

$$d[\text{ODI}]/dt = k_1[\text{TRI}] - k_3[\text{ODI}] \quad (2)$$

TABLE I  
Characteristics of data treatment

Compound	GLC <sup>a</sup>		<i>R</i> <sup>b</sup> , %	<i>k</i> <sub>error</sub> <sup>c</sup> , rel.%	[SDMA] <sup>d</sup>	[RX] <sup>d</sup>
	A	B				
C <sub>6</sub> H <sub>6</sub>	1.01	0	–	–	–	–
ClC <sub>6</sub> H <sub>5</sub>	1.19	0.024	17	4	0.55	0.35
Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>						
1,2-	1.75	–0.030	30	17	0.90	0.30
1,3-	1.90	–0.021	18	19	0.90	0.30
1,4-	1.82	–0.027	22	8	0.90	0.30
Cl <sub>3</sub> C <sub>6</sub> H <sub>3</sub>						
1,2,3-	2.32	–0.011	98	16	1.01	0.23
1,2,4-	1.92	0	67	21	1.01	0.23
Cl <sub>4</sub> C <sub>6</sub> H <sub>2</sub>						
1,2,4,5-	1.33	–0.055	99	16	1.10	0.19
Cl <sub>5</sub> C <sub>6</sub> H	1.0 <sup>e</sup>	–	100	<sup>f</sup>	1.17	0.16
BrC <sub>6</sub> H <sub>5</sub>	1.35	0	–	–	–	–
BrClC <sub>6</sub> H <sub>4</sub>						
1,2-	1.31	0	85	12	0.87	0.29
1,4-	1.29	0	80	14	0.87	0.29
Br <sub>2</sub> C <sub>6</sub> H <sub>4</sub>						
1,3-	1.40	0	100	15	0.83	0.28
1,4-	1.35	0	100	14	0.83	0.28

<sup>a</sup> Parameters of GLC calibration curves, where  $[\text{RX}]_{\text{actual}} = (P_{\text{RX}}/(P_{\text{ST}}+P_{\text{RX}})) [A + B (P_{\text{RX}}/(P_{\text{ST}}+P_{\text{RX}}))]$  (weight concentration). <sup>b</sup> *R* Maximum conversion to which the given dehalogenation was followed and the obtained results treated. <sup>c</sup> The relative error of the rate constant determination. <sup>d</sup> In mol l<sup>–1</sup>. <sup>e</sup> GC-MS method, see Experimental. <sup>f</sup> The rate constants calculated from the Arrhenius plot (see note <sup>a</sup> in Table III). The correlation coefficients were 0.847 and 0.935 for formation of 1,2,3,5- and 1,2,4,5-tetrachlorobenzene, respectively.

$$d[\text{MDI}]/dt = k_2[\text{TRI}] - k_4[\text{MDI}] \quad (3)$$

$$d[\text{CLP}]/dt = k_3[\text{ODI}] + k_4[\text{MDI}] - k_5[\text{CLP}] \quad (4)$$

$$d[\text{BEN}]/dt = k_5[\text{CLP}] \quad (5)$$

The subscripts denote the corresponding reaction steps. Concentrations of the above compounds are given as molar fractions in the sum of the starting substrate and all the products. SDMA was taken in such an excess that its concentration changes during the experiment could be neglected. Thus, the computed rate constants  $k$  were divided by the square root of SDMA concentration, in accordance with the determined kinetics of the reaction, documented by data collected in Table II (cf. Eq. (6),  $k_p$  in  $\text{mol}^{-0.5} \text{ l}^{0.5} \text{ min}^{-1}$ ). Comparison of experimental and computed data is shown in Fig. 1 for dehalogenation of 1,2,3-trichlorobenzene as an example. The values of both constants are given in Tables III and IV. The relative error in the rate constant determinations ( $k_{\text{error}}$  in rel.%) was calculated from at least two measurements and is given in Table I. In the analysis of data on dehalogenation of tetrachloro- and pentachlorobenzene, the average rate constants of dehalogenation of chlorobenzene to benzene and of dichlorobenzenes to chlorobenzene, respectively, were used to simplify the computation. These constants are given in Table IV in parentheses.

TABLE II

Determination of the reaction order in SDMA in initial phases of the dehalogenation of 1,2,4,5-tetrachlorobenzene and 1,2,3-trichlorobenzene. For reaction conditions see Experimental

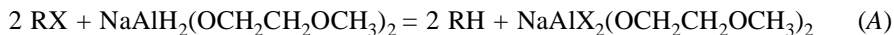
Compound	[SDMA] <sup>a</sup>	-[RX]/dt <sup>b</sup>
1,2,4,5-Cl <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	1.10	0.238
	0.61	0.180
	0.46	0.160
	0.34	0.136
Reaction order 0.475 ( $f^c = 0.9899$ )		
1,2,3-Cl <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1.10	0.115
	0.60	0.088
	0.46	0.067
	0.34	0.046
Reaction order 0.499 ( $f^c = 0.9695$ )		

<sup>a</sup> In  $\text{mol l}^{-1}$ . <sup>b</sup> The rate of the chloro compound consumption followed in the first 5 min of the reaction for the tetra- and in the first 2 min for the trichlorobenzene. <sup>c</sup>  $f$  Correlation coefficient of the least squares treatment.

## RESULTS AND DISCUSSION

*Stoichiometry of Dehalogenation by SDMA*

The first question which arises in connection with the title hydride is stoichiometry of studied dehalogenation reactions. It has been reported<sup>13</sup> that the reduction of organic halides RX to the corresponding hydrocarbons using SDMA can be expressed by Eq. (A) (cf. ref.<sup>19</sup>).



However, the inspection of literature data on SDMA dehalogenation (ref.<sup>19</sup> and Table I on p. 60 in ref.<sup>20</sup>) do not offer a proof for this assumption. The high preparative yields of the hydrocarbons were obtained exceptionally, and always with the hydride to hydrocarbon molar ratio exceeding several times the suggested stoichiometry. On using the reactants near to stoichiometric amounts, the reaction did not go to completion. To our knowledge no attempt has been made in the latter case to follow conversion of an organic halide parallel to the hydride consumption. As to the series of the hydrocarbons under study, the low reactivity of chlorobenzene toward SDMA (ref.<sup>20</sup> reports 2% yield of benzene at 110 °C (1 h), using SDMA/chlorobenzene molar ratio 1.35) predetermined the latter approach as the only feasible way of the elucidation of this question. Due to the suitable reactivity, we chose pentachlorobenzene for the above purpose.

The experiment carried out with equimolar amounts of both compounds showed that after 2 h-reaction at 70 °C, the pentachlorobenzene conversion was 56%, giving a mixture of 43% of tetrachlorobenzenes, 11% of trichlorobenzenes and 2% of dichlorobenzenes. Further prolongation of the reaction time to 4 h resulted in only small increase of pentachlorobenzene conversion (to 59%), yielding 44% of tetrachloro-, 13% of tri-

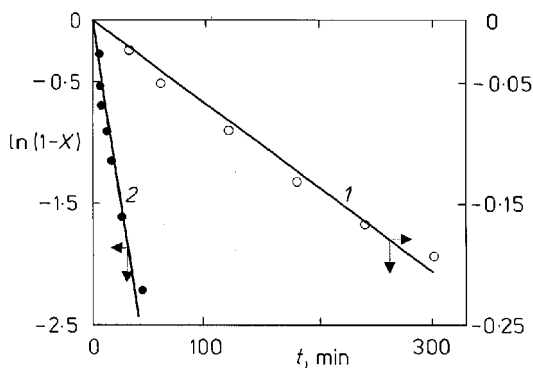
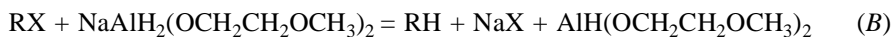


FIG. 1

Pseudo-first order kinetics of dehalogenation of chlorobenzene (1) and pentachlorobenzene (2) by SDMA. Reaction conditions: 1 [SDMA] = 0.55 mol l<sup>-1</sup>, [C<sub>6</sub>H<sub>5</sub>Cl] = 0.35 mol l<sup>-1</sup>, 70 °C, toluene; 2 [SDMA] = 1.16 mol l<sup>-1</sup>, [C<sub>6</sub>HCl<sub>5</sub>] = 0.15 mol l<sup>-1</sup>, 20 °C, toluene

chloro- and 2% of dichlorobenzenes. As found by parallel determination, the hydride consumption comports with these changes (a total of 0.82 mol of chlorine was transformed into  $\text{Cl}^-$  ion with the consumption of 0.92 mol of the SDMA hydrogen). Comparison of these data together with the fact that after this period the reaction proceeded further at a negligible rate documents that at least in the case of aryl chlorides only one hydrogen atom per SDMA molecule participates in the reaction. The reason could be the much reduced dehalogenation power of the aluminum monohydride formed (Eq. (B)).



### Kinetics of SDMA Dehalogenation

The second question to be answered is kinetics of the reaction. For this purpose, the course of the dehalogenation of each of the studied compounds was analyzed in terms of time changes in concentrations of the starting chlorobenzene and dehalogenation products. In order to simplify the treatment of obtained data, SDMA had been used in such a molar excess with respect to the chloro compound which made it possible to disregard its concentration changes. The validity of the pseudo-first order kinetics nearly up to maximum conversions followed (see  $R$  values in Table I) is documented on two examples in Fig. 1, including the least reactive and one of the most reactive substrates (chlorobenzene and pentachlorobenzene).

In each kinetic run, the time-concentration dependences for all the halogenated reaction components were fitted by a model consisting of a set of single consecutive and irreversible steps, as illustrated by the dehalogenation of 1,2,3-trichlorobenzene as an example in Experimental. The fit of experimental data to computed concentration-time

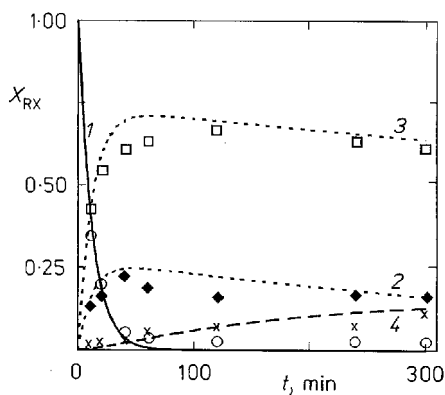


FIG. 2

Comparison of experimental (points) and computed (curves) data for dehalogenation of 1,2,3-trichlorobenzene (1,  $\circ$ ) to 1,2- (2,  $\blacklozenge$ ) and 1,3-dichlorobenzene (3,  $\square$ ), and chlorobenzene (4,  $\times$ ) (benzene formation omitted). For SDMA and RX concentrations see Table I, toluene, 70 °C. Rate constants  $k_p$  given in Table III. Mean standard deviations are 0.053  $X$  (1), 0.038  $X$  (2), 0.034  $X$  (3), and 0.022  $X$  (4)

curves was compared for different reaction orders in the chloro compounds. We have found that in all cases the fit (as based on the sum of squared deviations) was best for the first order in the chloro compound. The range of the conversions followed for each compound and taken subsequently to computation is summarized in Table I.

The reaction order in the hydride has been determined by following the rate of dehalogenation of two selected chlorobenzenes (1,2,4,5-tetrachlorobenzene and 1,2,3-trichlorobenzene) in dependence on SDMA concentration (Table II). In both cases, the slopes of the logarithmic rate vs [SDMA] plots close to 0.5 provide evidence for the half order of the reaction in the hydride.

The above findings show that the dehalogenation obeys the following simple rate equation:

$$-d[\text{RX}]/dt = k_p [\text{RX}] [\text{SDMA}]^{1/2}. \quad (6)$$

Although comparison with dehalogenations by other hydrides would be of interest in this connection, because of lack of relevant data, it could hardly be made with definite conclusions. This can be demonstrated on the early study<sup>11</sup> of dechlorination of a similar series of chlorobenzenes by  $\text{LiAlH}_4$  where the order in chloro compound was determined for only one derivative (1,2,3-trichlorobenzene, being also first order as above) while no attempt has been made to find the order of the dehalogenation in the aluminum hydride. The conversion vs time data analysis yielded the set of rate constants for the dehalogenation of each member of the series to the derivative containing by one less chlorine atom (further referred to as the first step dehalogenation), regardless of the isomer product distribution, as well as the set of rate constants of the dehalogenation to individual isomers. These are listed in Table III. For comparative purposes, all the measurements were performed at the temperature (70 °C) which was chosen as the compromise forced by the wide range of reactivities of the model compounds. The only exception was pentachlorobenzene, the extreme reactivity of which under above conditions made the analysis of withdrawn samples inaccurate. For that reason, its dehalogenation was examined at three different temperatures (20, 30, and 40 °C). As the optimized rate constants for the dehalogenation to individual isomers obeyed well Arrhenius relation, the rate data for standard temperature 70 °C were obtained from this dependence (Table III, footnote <sup>a</sup>).

### *Reaction Course and Structure–Reactivity Relations*

Inspection of Table III shows that the rate of the dehalogenation increases by more than four orders of magnitude on going from chlorobenzene to the pentachloro derivative, i.e. parallel to the increasing number of chlorine atoms in the chlorobenzenes.

The activating effect of the overall electron-withdrawing chlorine substituents compares with the character of the dehalogenation as the nucleophilic aromatic substitution



in which formation of the reaction intermediate is likely the rate determining step<sup>21,22</sup>. As for SDMA, such a mechanism was already postulated on the basis of Hammett correlation obtained for the dehalogenation of a series of monosubstituted chlorobenzenes with this hydride<sup>14,23</sup>, using the method of competitive reactions.

The reaction sequence for dehalogenation of studied series of chlorobenzenes, as found by analysis of the isomer distribution (see Experimental), is shown in Scheme 2.

TABLE III

Rate constants  $k$  ( $\text{min}^{-1}$ ) and  $k_p$  ( $\text{mol}^{-0.5} \text{l}^{0.5} \text{min}^{-1}$ , Eq. (6)) for the dehalogenation by SDMA. For reaction conditions see Experimental

Compound	$k \cdot 10^3$	$k_p \cdot 10^{3,a}$	Product
Chlorobenzenes			
$\text{ClC}_6\text{H}_5$	0.6	0.81	$\text{C}_6\text{H}_6$
1,2- $\text{Cl}_2\text{C}_6\text{H}_4$	1.6	1.7	$\text{ClC}_6\text{H}_5$
1,3- $\text{Cl}_2\text{C}_6\text{H}_4$	1.5	1.6	$\text{ClC}_6\text{H}_5$
1,4- $\text{Cl}_2\text{C}_6\text{H}_4$	1.1	1.2	$\text{ClC}_6\text{H}_4$
1,2,3- $\text{Cl}_3\text{C}_6\text{H}_3$	35.0	35.0	1,2- $\text{Cl}_2\text{C}_6\text{H}_4$
	70.0	70.0	1,3- $\text{Cl}_2\text{C}_6\text{H}_4$
1,2,4- $\text{Cl}_3\text{C}_6\text{H}_3$	0.7	0.7	1,2- $\text{Cl}_2\text{C}_6\text{H}_4$
	1.3	1.3	1,3- $\text{Cl}_2\text{C}_6\text{H}_4$
	4.3	4.3	1,4- $\text{Cl}_2\text{C}_6\text{H}_4$
1,2,3,5- $\text{Cl}_4\text{C}_6\text{H}_2$	750	720	1,3,5- $\text{Cl}_3\text{C}_6\text{H}_3$
	1 500	1 400	1,2,3- $\text{Cl}_3\text{C}_6\text{H}_3$
	max. 0.1		1,2,4- $\text{Cl}_3\text{C}_6\text{H}_3$
1,2,4,5- $\text{Cl}_4\text{C}_6\text{H}_2$	970	920	1,2,4- $\text{Cl}_3\text{C}_6\text{H}_3$
$\text{Cl}_5\text{C}_6\text{H}^b$	91	84	1,2,3,5- $\text{Cl}_4\text{C}_6\text{H}_2$
	1 400	1 300	1,2,4,5- $\text{Cl}_4\text{C}_6\text{H}_2$
Bromochlorobenzenes			
1,2- $\text{BrClC}_6\text{H}_4$	870	930	$\text{ClC}_6\text{H}_5^c$
1,4- $\text{BrClC}_6\text{H}_4$	260	280	$\text{ClC}_6\text{H}_5^c$
Bromobenzenes			
1,3- $\text{Br}_2\text{C}_6\text{H}_4$	1 600	1 800	$\text{BrC}_6\text{H}_5$
1,4- $\text{Br}_2\text{C}_6\text{H}_4$	1 500	1 600	$\text{BrC}_6\text{H}_5$

<sup>a</sup>  $k_p = k [\text{SDMA}]^{-0.5}$ . <sup>b</sup> The values for the temperature 70 °C calculated from the Arrhenius plot, using the following  $k$ 's:  $k \cdot 10^3, \text{min}^{-1}$  for 1,2,3,5- $\text{Cl}_4\text{C}_6\text{H}_2 = 16.5$  (20 °C), 34 (30 °C), and 43 (40 °C) and for 1,2,4,5- $\text{Cl}_4\text{C}_6\text{H}_2 = 150$  (20 °C), 330 (30 °C), and 380 (40 °C). <sup>c</sup> Any dechlorination to bromobenzene has not been detected.

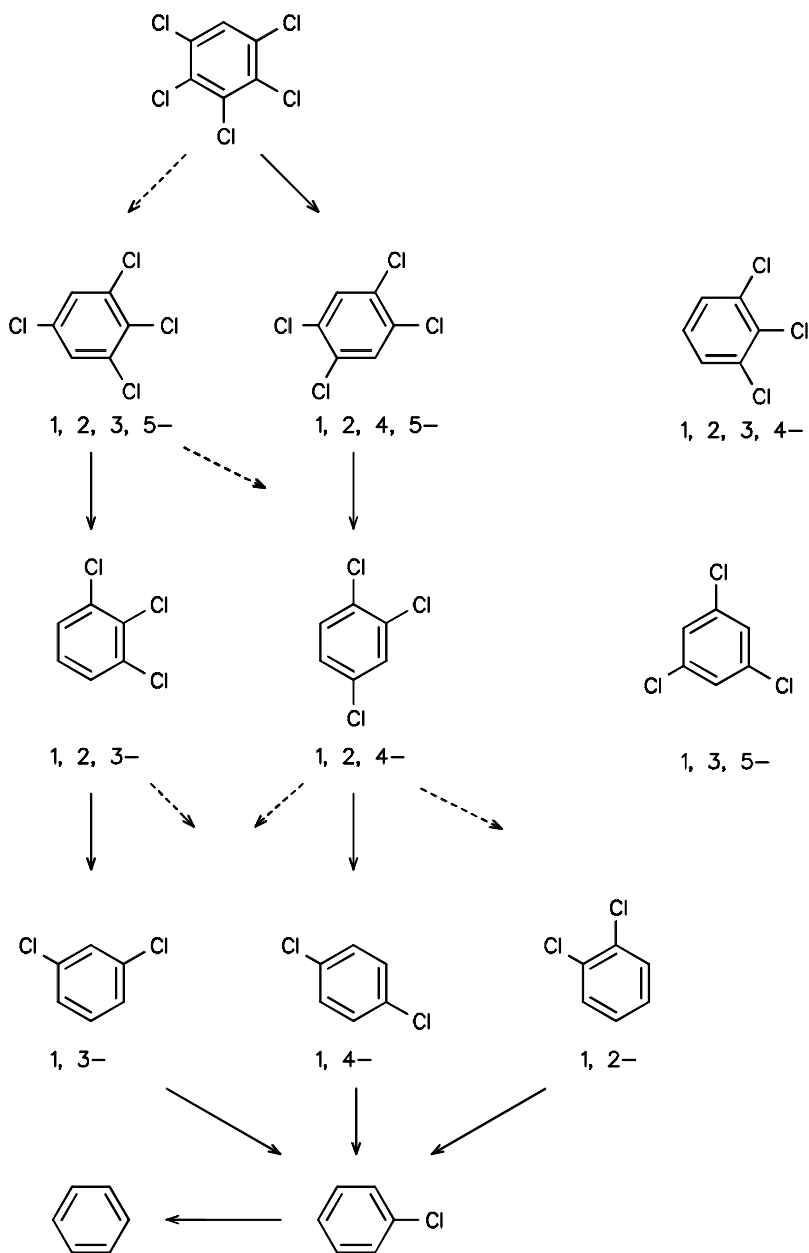
The preferred dehalogenation paths are designated by solid arrows. For clarity, the rate constants corresponding to single dehalogenation steps are not presented in Scheme 2, and the reader is referred to Tables III and IV for this information.

The results can be discussed from several aspects. First, their comparison with data reported<sup>11</sup> for  $\text{LiAlH}_4$  is of interest. For this purpose the relevant kinetic data were converted into total relative reactivities,  $k_{\text{rel}}$ , taking chlorobenzene as the reference (Table V). For the higher chlorinated compounds, also partial  $k_{\text{rel}}$  were calculated, in order to characterize the relative ease with which these compounds yield individual isomers in the first step of the dehalogenation (Table V). Inspection of data in Table V leads to the following conclusions: (i) Similarly to SDMA, also with  $\text{LiAlH}_4$  the reactivity of the chloro compounds increases with their increasing chlorine substitution. In both cases this increase covers a similar reactivity range (i.e. slightly over three orders of magnitude). (ii) Similar behaviour of both hydrides is documented also by their similar selectivity (compare partial  $k_{\text{rel}}$  for the chloro compounds of the series and the

TABLE IV  
Rate constants  $k$  ( $\text{min}^{-1}$ ) and  $k_{\text{p}}$  ( $\text{mol}^{-0.5} \text{l}^{0.5} \text{min}^{-1}$ , Eq. (6)) computed from multistep dehalogenations

Dehalogenated substrate	$k \cdot 10^3$	$k_{\text{p}} \cdot 10^3$	Product
Chlorobenzene from			
1,2- $\text{Cl}_2\text{C}_6\text{H}_4$	3.9	4.1	benzene
1,3- $\text{Cl}_2\text{C}_6\text{H}_4$	2.1	2.2	benzene
1,4- $\text{Cl}_2\text{C}_6\text{H}_4$	1.4	1.5	benzene
$\text{Cl}_2\text{C}_6\text{H}_4$	(2.5) <sup>a</sup>	(2.6)	benzene
$\text{Cl}_3\text{C}_6\text{H}_3$	(4.4) <sup>a</sup>	(4.4)	benzene
1,2- $\text{BrClC}_6\text{H}_4$	4.3	4.6	benzene
1,2-Dichlorobenzene from			
$\text{Cl}_3\text{C}_6\text{H}_3$	(6.0) <sup>a</sup>	(6.0)	chlorobenzene
1,3-Dichlorobenzene from			
$\text{Cl}_3\text{C}_6\text{H}_3$	(1.7) <sup>a</sup>	(1.7)	chlorobenzene
1,4-Dichlorobenzene from			
$\text{Cl}_3\text{C}_6\text{H}_3$	(1.2) <sup>a</sup>	(1.2)	chlorobenzene
Bromobenzene from			
1,3- $\text{Br}_2\text{C}_6\text{H}_4$	12	13	benzene
1,4- $\text{Br}_2\text{C}_6\text{H}_4$	5.5	6.0	benzene

<sup>a</sup> Average values used in the analysis of data on dehalogenations of penta- and tetrachlorobenzenes (see Treatment of data in Experimental).



SCHEME 2

structure of the formed isomers). The only exception, so far not explained, is the course of the dehalogenation of 1,2,3,5-tetrachlorobenzene that, in addition to the common trichloro isomer, 1,3,5-trichlorobenzene, yields 1,2,3-trichlorobenzene with SDMA, and 1,2,4-trichlorobenzene with  $\text{LiAlH}_4$ . (iii) The reactivity increase upon stepwise substitution (compare the most reactive di-, tri-, tetra-, and pentachloro compounds) indicates non-additivity of the effects of chlorine groups. The observed "saturation effect" becomes even more evident when correction is made for statistical factors (i.e. the total reactivity of a given compound is divided by the number of reaction sites (C-Cl bonds), for more detailed discussion of this approach see ref.<sup>24</sup>).

As the above mentioned trend can result from the action of both polar and steric effects, let us analyze relative role of both effects, starting with the dichlorinated com-

TABLE V  
Relative reactivity of chlorobenzenes in their dehalogenation with SDMA and  $\text{LiAlH}_4$

Chloro compound	Total $k_{\text{rel}}^a$		Product <sup>b</sup>	Single $k_{\text{rel}}^c$	
	SDMA	$\text{LiAlH}_4$		SDMA	$\text{LiAlH}_4$
$\text{ClC}_6\text{H}_5$	1.0	1.0	H	1.0	1.0
1,2- $\text{Cl}_2\text{C}_6\text{H}_4$	2.1	1.8	Cl	2.1	1.8
1,3- $\text{Cl}_2\text{C}_6\text{H}_4$	2.0	2.3	Cl	2.0	2.3
1,4- $\text{Cl}_2\text{C}_6\text{H}_4$	1.5	1.1	Cl	1.5	1.1
1,2,3- $\text{Cl}_3\text{C}_6\text{H}_3$	129	52	1,2- $\text{Cl}_2$	43	32
			1,3- $\text{Cl}_2$	86	20
1,2,4- $\text{Cl}_3\text{C}_6\text{H}_3$	8.0	30	1,2- $\text{Cl}_2$	0.9	4.3
			1,3- $\text{Cl}_2$	1.6	5.7
			1,4- $\text{Cl}_2$	5.3	20
1,3,5- $\text{Cl}_3\text{C}_6\text{H}_3$	–	19	1,3- $\text{Cl}_2$	–	19
1,2,3,5- $\text{Cl}_4\text{C}_6\text{H}_2$	2 617	805	1,2,3- $\text{Cl}_3$	1 728	–
			1,2,4- $\text{Cl}_3$	–	382
			1,3,5- $\text{Cl}_3$	889	420
1,2,4,5- $\text{Cl}_4\text{C}_6\text{H}_2$	1 135	–	1,2,4- $\text{Cl}_3$	1 135	–
$\text{Cl}_5\text{C}_6\text{H}$	1 730	250	1,2,3,5- $\text{Cl}_4$	125	–
			1,2,4,5- $\text{Cl}_4$	1 605	1 250

<sup>a</sup> Total  $k_{\text{rel}}$  stands for the overall reactivity of the chloro compound in the first step of the reaction, yielding product(s) with one less chlorine atoms in the molecule. Data for SDMA calculated from Table III, those for  $\text{LiAlH}_4$  taken from ref.<sup>11</sup>. <sup>b</sup> The product abbreviation based on the chlorine atoms in the molecule (e.g. Cl stands for chlorobenzene, 1,2- $\text{Cl}_2$  for 1,2-dichlorobenzene etc.). <sup>c</sup> Single  $k_{\text{rel}}$ 's relate to the rates of formation of individual isomers (their sum gives the total  $k_{\text{rel}}$ ).

pounds. We believe that practically the same reactivity of the *ortho* and *meta* isomer ( $k_{\text{rel}} = 2.1$  for 1,2- and 2.0 for 1,3-dichlorobenzene, Table V) can be attributed solely to polar effects of chlorine atoms. It is noteworthy that similar situation was already observed in SDMA dehalogenation of chlorotoluenes<sup>14,23</sup> ( $k_{\text{rel}} = 0.10$  for 2-methyl-, 0.14 for 3-methyl-, and 0.12 for 4-methylchlorobenzene). As methyl substituent has similar steric demands as chlorine atom (cf. ref.<sup>25</sup> for more detailed discussion), this finding can be taken as an independent support for the above conclusion.

Based on data obtained in both reductions of the trichloro derivatives, steric effects do not play significant role in determining the reactivity of 1,2,3-isomer, which would otherwise decrease upon their action. By contrast, the additional *ortho* chlorine exerts the overall activating effect (stronger for SDMA, weaker for  $\text{LiAlH}_4$ , cf.  $k_{\text{rel}}$  for 1,2,3- $\text{Cl}_3\text{C}_6\text{H}_3$  in Table V) that enhances the reactivity of the 1,2,3-trichloro derivative above that of 1,2,4- and 1,3,5-isomers.

It is worthy of mentioning that the activation by the *ortho* chlorine is not specific for this reduction but it was also observed in the nucleophilic aromatic substitution of dichlorobenzene isomers with alcoholates and ascribed to inductive effects<sup>26</sup>.

Comparison of partial relative rates of dehalogenation of 1,2,3- and 1,2,4-trichlorobenzenes shows that the reaction of the 1,2,4-trichloro derivative with both hydrides has similar selectivity pattern (partial  $k_{\text{rel}}$  sequence: 1,4- $\text{Cl}_2 > 1,3\text{-Cl}_2 > 1,2\text{-Cl}_2$ , Table V). On the other hand, the dehalogenation of 1,2,3-trichlorobenzene with  $\text{LiAlH}_4$  gives isomer distribution very close to that expected on the basis of statistical considerations (two equivalent positions 1 and 3 vs one internal position 2 would give 1,2-dichlorobenzene in 2 : 1 ratio with respect to 1,3-dichloro isomer), while SDMA prefers 1,3-dichlorobenzene formation. As partial  $k_{\text{rel}}$ 's for  $\text{LiAlH}_4$  dehalogenation were calculated from isomer distribution at 50% trichlorobenzene conversion (cf. ref.<sup>11</sup>), we made kinetic experiment (2 – 3 mmol 1,2,3-trichlorobenzene, 15 ml THF, 63 °C,  $\text{LiAlH}_4$  :  $\text{Cl}_3\text{C}_6\text{H}_3$  molar ratio = 2.3 : 1) with the aim to determine actual rates of formation of both isomers. The results obtained ( $k = 2.2 \cdot 10^{-3} \text{ min}^{-1}$  for 1,2-, and  $6.7 \cdot 10^{-4} \text{ min}^{-1}$  for 1,3-dichlorobenzene formation) confirmed the above selectivity difference.

The higher reactivity of the C–Cl bonds in 1,2,3-arrangement reflects also in the higher overall rate of dehalogenation of 1,2,3,5-tetrachlorobenzene compared to the 1,2,4,5- $\text{Cl}_4$  isomer (cf.  $k_{\text{rel}}$  in Table V). As already mentioned in connection with general comparison of behaviour of both hydrides,  $\text{LiAlH}_4$  attacks positions 1 and 2 giving both 1,3,5- and 1,2,4-trichlorobenzene isomers at similar rates (Table V) while SDMA attack is oriented unexpectedly also to position 5, even preferentially to position 1.

Of three possible tetrachloro compounds (1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrachlorobenzenes), dehalogenation of pentachlorobenzene with both hydrides gives almost selectively 1,2,4,5-tetrachlorobenzene. The other isomer formed only in the case of SDMA reaction (and at the more than by one order of magnitude slower rate) was 1,2,3,5-tetrachlorobenzene. The course of the dehalogenation of pentachlorobenzene

further indicates that even in this substrate, in which the already mentioned saturation could lead to levelling of substituent effects, the isomer distribution is not solely due to statistical factors (these predict 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrachlorobenzenes in 2 : 2 : 1 ratio). However, whether (and to which extent) the overall lower reactivity of pentachlorobenzene compared to the most reactive tetrachlorobenzene (compare  $k_{\text{rel}}$  for the 1,2,3,5-tetrachloro derivative in Table V) can be ascribed to steric effects cannot at present be decided.

Notwithstanding, the results obtained with the lower chlorinated benzenes do not speak for generally important role of steric factors in both dehalogenations.

### *Specific Benzene Formation in Multistep Dehalogenations*

Finally, kinetic analysis revealed an unexpected course of formation of the end product, benzene, in the case of exhaustive dehalogenation of the higher chlorinated benzenes (further referred to as multistep dehalogenation), in that it is produced from chlorobenzene (as the reaction intermediate, see Scheme 2) at faster rate than in the reaction of chlorobenzene as such. Furthermore, there is a distinct dependence on the structure of the higher-chlorinated derivative subjected to multistep dehalogenation. This can be best illustrated by data on dehalogenation of dichlorobenzenes (Table IV). They show that while the mentioned rate enhancement is observed with all isomers, it is greatest in the case of the *o*-dichlorobenzene.

An analogous situation has been encountered also in the dehalogenation of dibromobenzenes (Table IV). Thus, while both isomers (1,3- and 1,4-) are debrominated to bromobenzene at similar rates, the product of the exhaustive debromination, benzene, is formed at twice faster rate from the *meta* than the *para* isomer.

We believe that the most likely explanation of these findings is the assumption that the dehalogenation of polyhalogenated hydrocarbons does not proceed exclusively via steps in which interaction of SDMA with the substrate leads to the cleavage of only one carbon-halogen bond, but that in certain number of events two hydride atoms of

TABLE VI

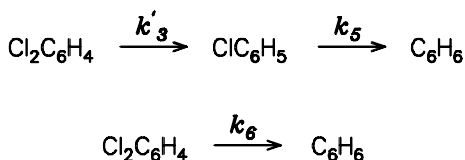
Rate constants for dechlorination of dichlorobenzene isomers with participation of the single step dehalogenation to benzene (Scheme 3)

$\text{Cl}_2\text{C}_6\text{H}_4$	$k'_3 \cdot 10^{3,a}$	$k_5 \cdot 10^{3,a}$	$k_6 \cdot 10^{3,a}$	$k_6/k'_3$
1,2-	1.15	0.62	0.56	0.48
1,3-	1.02	0.62	0.19	0.18
1,4-	1.03	0.62	0.080	0.08

<sup>a</sup> For definition of the rate constants (in  $\text{mol}^{-0.5} \text{l}^{0.5} \text{min}^{-1}$ ) see Scheme 3.

SDMA participate in formation of the reaction intermediate. This would result in the single step cleavage of two carbon-halogen bonds. To check this idea, we made an attempt to apply this model, using dehalogenation of dichlorobenzene isomers as the simplest example (Scheme 3, SDMA omitted for clarity).

The results computed with the  $k_5$  constant obtained for the dehalogenation of chlorobenzene ( $k_p = 0.62 \text{ mol}^{-0.5} \text{ l}^{0.5} \text{ min}^{-1}$ , Table III) are summarized in Table VI. The



SCHEME 3

relative extent to which the single step dehalogenation ( $k_6$ ) competes with the two step process ( $k'_3$ ,  $k_5$ ) can be expressed by  $k_6/k'_3$  ratio. The magnitude of  $k_6/k'_3$ 's suggests that the single step dehalogenation plays a significant role especially in the dehalogenation of the *ortho* isomer. We believe that this difference cannot be attributed to changes in polar effects solely (compare Hammett sigma constants<sup>24</sup> for *meta* and *para* Cl) but that the single step dehalogenation reflects likely the increased accessibility of the two adjacent C-Cl bonds for formation of the reaction intermediate with SDMA. However, at present no additional experimental evidence is available to corroborate the above proposed model and/or to postulate the structure of this intermediate.

Notwithstanding, the present study has provided further support for the assumption<sup>14,23</sup> that the dehalogenation with SDMA proceeds as a nucleophilic aromatic substitution in which formation of the reaction intermediate is the rate determining step of the reaction. Furthermore, the isomer distribution and rate data analysis made it possible to propose a more detailed reaction sequence for the studied dehalogenation and to contribute to the recognition of competitive dehalogenation steps. Their role is under further investigation.

## SYMBOLS

BEN	benzene
CLP	chlorobenzene
ITD	ion trap detector
MDI	1,3-dichlorobenzene
ODI	1,2-dichlorobenzene
PCB	polychlorobiphenyls
RX	halogenated compound

SDMA	sodium dihydridobis(2-methoxyethoxo)aluminate
TRI	1,2,3-trichlorobenzene
$k$	rate constant, $\text{min}^{-1}$
$k_{\text{error}}$	relative error in $k$ determination, rel. %
$k_i$	rate constant of $i$ -th step of the dehalogenation
$k_p$	rate constant in Eq. (6), $\text{mol}^{-0.5} \text{l}^{0.5} \text{min}^{-1}$
$t$	reaction time, min
$X$	molar fraction

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