

# The kinetics of the aluminium bromide catalyzed isomerization of 1-propyl bromide

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## Abstract

An analysis of the initial rates of reaction was carried out of the aluminium bromide catalyzed isomerization of 1-propyl bromide:  $1\text{-C}_3\text{H}_7\text{Br} + \text{Al}_2\text{Br}_6 = 2\text{-C}_3\text{H}_7\text{Br} + \text{Al}_2\text{Br}_6$ . The proposed kinetics of the process is consistent with a nucleophilic displacement of the aliphatic bromine contained in complexes of the alkyl bromide with aluminium bromide. The displacement, initiated by the  $\text{AlBr}_4^-$  ion, is accompanied by a rate determining 2,1 hydride shift.

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*Keywords:* Aluminium bromide; Isomerization; Lewis acid; Nucleophilic substitution; 2,1 hydride shift

## 1. Introduction

The aluminium bromide catalyzed isomerization of 1-propyl bromide can be described as a Wagner–Meerwein rearrangement of the primary carbocation [1]. The carbocation is assumed to result from the dissociation of a complex of the aluminium bromide and the alkyl bromide and the rearrangement of the alkyl chain is attributed to a hydride shift in the carbocation. The rearrangement itself should accordingly be of first order in the alkyl halide when the dissociation is the rate determining step or half order when the hydride shift is the slowest reaction.

Research into the aluminium halide catalyzed isomerization of 1-propyl bromide in an aprotic solvent showed however a complex mechanism depending on the concentration of the reagents which could not be resolved at the time [2]. A similar effect of the ratio of reagents on the reaction kinetics was later found in the metal bromide catalyzed bromine exchange reaction with alkyl halides [3].

The aluminium bromide catalyzed isomerization of 1-propyl bromide in  $\text{CS}_2$  solvent, the subject of the present paper, offers the opportunity to analyze the initial reaction equation and the resulting reaction mechanism over a large range of concentrations up to 80% conversions.

The investigation of the isomerization process involves a multiple regression analysis of the initial rates of reaction and is followed by a proposed kinetic interpretation of the results and a comparison of the calculated and experimental isomerization data. The result of the analysis is discussed. Details of the analysis and calculations are presented in the supplement together with the experimental data.

## 2. Experimental

The experiments were carried out under dry nitrogen. The reaction was stopped by discharging a small amount of the sample of the reaction mixture in a concentrated solution of sodium bromide in water at  $-20^\circ\text{C}$ . The alkyl bromide concentrations of 1-propyl bromide and 2-propyl bromide were measured by infra red analysis using calibration curves. Details of the experiments and calculations are presented in the supplement.

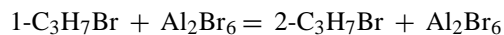
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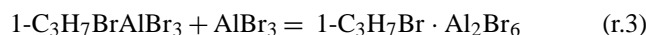
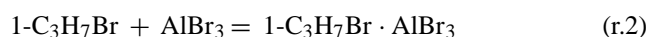
### 3. Results and discussion

#### 3.1. Results

The isomerization reaction is presented by:



The initial rate of this reaction is a function of the reaction components, i.e.  $V_0 = f\{(\text{Al}_2\text{Br}_6)(1\text{-C}_3\text{H}_7\text{Br})\}$ . The method of analysis involves a linear regression calculation of the logarithms of the initial rates and concentration of the components. The monomeric complex,  $1\text{-C}_3\text{H}_7\text{Br}\cdot\text{AlBr}_3$  [4] and the expected dimeric complex,  $1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6$ , are themselves a function of  $\text{Al}_2\text{Br}_6$  and  $1\text{-C}_3\text{H}_7\text{Br}$  and as such implied in the result of the analysis. The following components are present at the start of the reaction<sup>1</sup>:



The equilibria are rapidly attained, irrespective of the initial complexing step, i.e.  $1\text{-C}_3\text{H}_7\text{Br}$  with  $\text{AlBr}_3$ , or with  $\text{Al}_2\text{Br}_6$  or both.

The multiple regression analysis of the initial rates of the aluminium bromide catalyzed isomerization of 1-propyl bromide, which is described in detail in the supplement, resulted in the following rate equation:

$$V_0 = -d(1\text{-C}_3\text{H}_7\text{Br}/dt) \approx a(1\text{-C}_3\text{H}_7\text{Br})^{1.5}(\text{Al}_2\text{Br}_6) + b(1\text{-C}_3\text{H}_7\text{Br})^{1.5}(\text{Al}_2\text{Br}_6)^{1.5} + c(1\text{-C}_3\text{H}_7\text{Br})^{2.5}(\text{Al}_2\text{Br}_6)^{2.5} \quad (1)$$

Considering the reactions (r.1)–(r.3) for the expressions of the complexes and substituting values for the coefficients as presented in the supplement the following rate equation results:

$$V_0 = 0.0060 \times (1\text{-C}_3\text{H}_7\text{Br}\cdot\text{AlBr}_3)(1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6)^{0.5} + 0.359 \times (1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6)(1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6)^{0.5} + 1540 \times (1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6)^2(1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6)^{0.5} \quad (2)$$

The relation of the experimental and calculated rates is shown in Fig. 1 which is a plot of  $\ln V_{0,\text{exp}} = 0.99991 \ln V_{0,\text{calc}} + 5 \times 10^{-6}$ .

All three terms of Eq. (2) contain the factor  $(1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6)^{0.5}$  representing the expression for the concentration of the  $\text{AlBr}_4^-$  ion resulting from the dissociation of  $1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6$ :

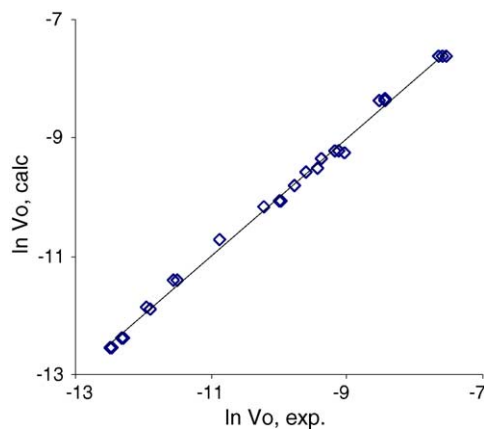
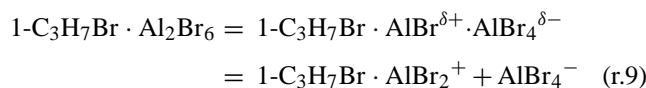
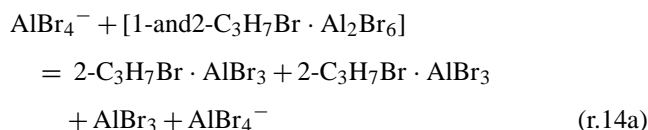
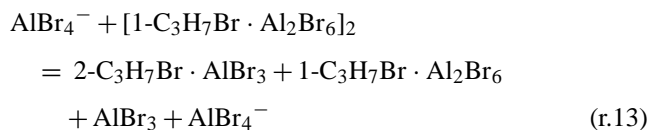
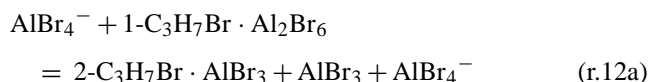
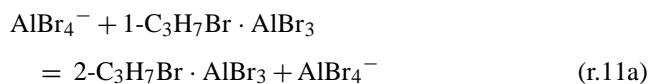


Fig. 1. Experimental vs. calculated initial isomerization rates of reaction.

The first two terms of Eq. (2) describe a displacement of the bromine from 1-propyl bromide in  $1\text{-C}_3\text{H}_7\text{Br}\cdot\text{AlBr}_3$  and  $1\text{-C}_3\text{H}_7\cdot\text{Al}_2\text{Br}_6$  complexes by the  $\text{AlBr}_4^-$  ion. The displacement is accompanied by the rate determining hydrogen shift in a three membered carbenium transition state [2,4].

The expression of  $(1\text{-C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6)^2$  in the third term of Eq. (2) can be tentatively interpreted as a dipole–dipole association of two highly polarized molecules,  $[1\text{-C}_3\text{H}_7\text{Br}\cdot\text{AlBr}_2^{\delta+}\cdot\text{AlBr}_4^{\delta-}]_2$  in the apolar  $\text{CS}_2$  solvent. The dipole moments of  $\text{AlBr}_3$  complexes with water, alcohols and ethers are of the order of 7D [5]. The tendency of the  $\text{C}_3\text{H}_7\text{Br}\cdot\text{Al}_2\text{Br}_6$  complexes to dissociate would indicate a similar dipole moment and dipole–dipole associations can be expected in apolar solvents.

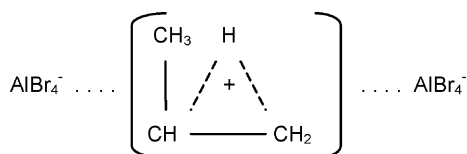
The isomerization of 1-propyl bromide would seem to be the result of a displacement reaction by  $\text{AlBr}_4^-$  ions of the aliphatic bromide in complexes of the alkyl bromide with  $\text{AlBr}_3$  and  $\text{Al}_2\text{Br}_6$ . The latter is also contained in clusters of two molecules. The following reactions refer to the isomerization step:



<sup>1</sup> Numbers of the reactions are according to Table 1.

Table 1  
Reaction scheme of the isomerization of 1-C<sub>3</sub>H<sub>7</sub>Br in the presence of Al<sub>2</sub>Br<sub>6</sub>

Reactions	$k_f/k_b$
Complex and cluster formation	
1-C <sub>3</sub> H <sub>7</sub> Br + AlBr <sub>3</sub> = 1-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> (r.2)	1.29 × 10 <sup>6</sup> /10 l/mol
1-C <sub>3</sub> H <sub>7</sub> BrAlBr <sub>3</sub> + AlBr <sub>3</sub> = 1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> (r.3)	15000/10 l/mol
2-C <sub>3</sub> H <sub>7</sub> Br + AlBr <sub>3</sub> = 2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> (r.4)	3.4 × 10 <sup>6</sup> /10 l/mol
2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + AlBr <sub>3</sub> = 2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> (r.5)	17000/10 l/mol
1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> + 1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> = [1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> ] <sub>2</sub> (r.6)	1000/10 l/mol
1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> + 2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> = [1-and2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> ] (r.7)	1500/10 l/mol
2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> + 2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> = [2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> ] <sub>2</sub> (r.8)	2250/10 l/mol
Dissociation	
Al <sub>2</sub> Br <sub>6</sub> = AlBr <sub>3</sub> + AlBr <sub>3</sub> (r.1)	10/10 <sup>11</sup> mol/l
1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> = 1-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + AlBr <sub>3</sub> (r.9)	10/10 <sup>5</sup> mol/l
2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> = 2-C <sub>3</sub> H <sub>7</sub> BrAlBr <sub>2</sub> <sup>+</sup> + AlBr <sub>4</sub> <sup>-</sup> (r.10)	12/10 <sup>5</sup> mol/l
Isomerization	
AlBr <sub>4</sub> <sup>-</sup> + 1-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> = 2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.11a)	0.60 l/mol s
AlBr <sub>4</sub> <sup>-</sup> + 2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> = 1-C <sub>3</sub> H <sub>7</sub> BrAlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.11b)	0.03 l/mol s
AlBr <sub>4</sub> <sup>-</sup> + 1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> = 2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + AlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.12a)	35.9 l/mol s
AlBr <sub>4</sub> <sup>-</sup> + 2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> = 1-C <sub>3</sub> H <sub>7</sub> Br · Al + AlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.12b)	0.30
AlBr <sub>4</sub> <sup>-</sup> + [1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> ] <sub>2</sub> = 2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + 1-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> + AlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.13)	1540 l/mol s
AlBr <sub>4</sub> <sup>-</sup> + [1-and2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> ] = 2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + 2-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + AlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.14a)	1000 l/mol s
AlBr <sub>4</sub> <sup>-</sup> + [1-and2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> ] = 1-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + 1-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + AlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.14b)	4 l/mol s
AlBr <sub>4</sub> <sup>-</sup> + [2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> ] <sub>2</sub> = 1-C <sub>3</sub> H <sub>7</sub> Br · AlBr <sub>3</sub> + 2-C <sub>3</sub> H <sub>7</sub> Br · Al <sub>2</sub> Br <sub>6</sub> + AlBr <sub>3</sub> + AlBr <sub>4</sub> <sup>-</sup> (r.15)	6 l/mol s



A carbenium type transition state is the preferred rate determining step [4] in accordance with the hydrogen isotope effect observed with 2,2-dideutero-1-propyl bromide and 2-deutero-1-propyl bromide [2]. The complex scheme of the isomerization reactions is presented in Table 1. The agreement of the calculated curves with the experimental ones, as indicated by the average and relative deviation data in Table 3 shows that Eq. (2) represents the kinetics of the isomerization. The experimental and calculated reaction curves are presented in a simplified format in Fig. 3.

The contribution of the terms to the overall rate varies with the concentrations of aluminium bromide and 1-propyl bromide. The isomerization of the cluster, the (1-C<sub>3</sub>H<sub>7</sub>Br · Al<sub>2</sub>Br<sub>6</sub>)<sup>2.5</sup> term, is dominant for high (Al<sub>2</sub>Br<sub>6</sub>) and (1-C<sub>3</sub>H<sub>7</sub>Br) concentrations and the isomerization reaction of monomeric complex, the (1-C<sub>3</sub>H<sub>7</sub>Br · AlBr<sub>3</sub>) × (1-C<sub>3</sub>H<sub>7</sub>Br · Al<sub>2</sub>Br<sub>6</sub>)<sup>0.5</sup> term, contributes significantly at the lower concentrations of (Al<sub>2</sub>Br<sub>6</sub>) and (1-C<sub>3</sub>H<sub>7</sub>Br). The third term (1-C<sub>3</sub>H<sub>7</sub>Br · Al<sub>2</sub>Br<sub>6</sub>)<sup>1.5</sup> is accountable for 20–30% contribution in reactions with (1-C<sub>3</sub>H<sub>7</sub>Br)<sub>0</sub> < 0.2 mol/l and less for the reactions with (1-C<sub>3</sub>H<sub>7</sub>Br)<sub>0</sub> > 0.2 mol/l.

### 3.2. Data from literature

The isomerization experiments of Adema [4] were carried out at 24 °C and the initial reaction rates were obtained by microwave measurements. Calculating the initial concentra-

tions of the reagents at the start of the reaction according to the *K*-values at –19 °C and applying Eq. (2) to the results provides the initial reaction rates at –19 °C. A comparison of these rates with the rates at +24 °C should show a simple relationship determined by the temperature difference or activation energy only. The data for the initial rates satisfy the relation  $V_{0,-19} = (0.028 \pm 0.002) \times V_{0,+24} - 9.54 \times 10^{-3}$ . This relation is presented in Fig. 2.

The slope, 0.028, is a measure of the overall activation energy which is calculated to be 12.5 kcal/mol. This value compares well with the 12.2 kcal/mol [6].

The application of Eq. (2) to the experiments also shows that the isomerization at –19 °C depends for about 82% on the reaction of AlBr<sub>4</sub><sup>-</sup> with 1-C<sub>3</sub>H<sub>7</sub>Br · AlBr<sub>3</sub>, for 15% with 1-C<sub>3</sub>H<sub>7</sub>Br · Al<sub>2</sub>Br<sub>6</sub> and only for 3% with the 1-C<sub>3</sub>H<sub>7</sub>Br · Al<sub>2</sub>Br<sub>6</sub> clusters. This agrees with the conclusion of the authors where a reaction of the AlBr<sub>4</sub><sup>-</sup> ion with the 1-C<sub>3</sub>H<sub>7</sub>Br · AlBr<sub>3</sub> complex is presumed to be in accordance with

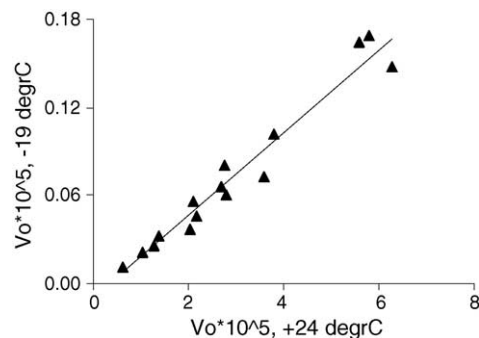


Fig. 2. Experimental rates at +24 °C and calculated rates at –19 °C, Eq. (2) of isomerization reactions from [4].

the results of the isomerization of 1-bromo-2-phenylethane-1 described previously by Adema and Sixma [7].

*Bromine exchange* experiments also showed a dependence of the reaction rates on the ratio of the antimony- and alkyl-bromides [3]. First order was observed for the alkyl halides and first or second order for the catalyst depending on the relatively low or high concentration of the metal halide. The exchange can be described as an internal shift of a bromine atom in the polarized  $\text{RBr}^{\delta+} \cdot \text{Sb}_2\text{Br}_6^{\delta-}$  complex for a relatively high concentration and a shift in the  $\text{RBr}^{\delta+} \cdot \text{SbBr}_3^{\delta-}$  complex for the lower catalyst concentration. Polar solvents, nitrobenzene and or 1,2,4-trichlorobenzene, and substrates like  $\alpha$ -phenylethyl bromide, benzyl bromide and *tert*-butyl benzene provide the environment for the required polarization of the complexes.

The reported bromine exchange of 1-propyl bromide and gallium bromide in 1,2,4-trichlorobenzene and nitrobenzene is first order in 1-propyl bromide and second order in gallium bromide only [8]. The rate determining reaction is assumed to be an internal bromine shift in the  $1\text{-C}_3\text{H}_7\text{Br}^{\delta+} \cdot \text{Ga}_2\text{Br}_7^{\delta-}$  complex. However, the observed reaction orders also fit the substitution reaction of labeled  $\text{GaBr}_4^-$  with the  $1\text{-C}_3\text{H}_7\text{Br} \cdot \text{GaBr}_3$  complex without a rearrangement step. The polarization of this complex could be well insufficient to allow an internal bromine shift.

### 3.3. Discussion

The analysis of the isomerization data revealed a complex rate equation. The earlier observation of different orders of reaction for different intake ratios [2] are confirmed. A similar effect was found by Sang Up Choi et al. [3] for the bromine exchange of antimony bromide and alkyl bromides where the relative concentration of the catalyst determined the order of the reaction.

The aluminium bromide catalyzed isomerization can be described as a concerted bimolecular rearrangement of the complexes of 1-propyl bromide initiated by the nucleophilic aluminium bromide ion.

In addition to the dative complexes  $1\text{-C}_3\text{H}_7\text{Br} \cdot \text{AlBr}_3$  and  $1\text{-C}_3\text{H}_7\text{Br} \cdot \text{Al}_2\text{Br}_7$  a third complex is proposed consisting of a bimolecular cluster of the highly polarized dimeric complex. The dipole moments of these complexes [5] indicate the feasibility of these clusters in the  $\text{CS}_2$  solvent. Whereas the clusterformation of two  $\text{C}_3\text{H}_7\text{Br} \cdot \text{AlBr}_3$  molecules or mixed clusters cannot be excluded, they would not seem to provide an energetic gain. The observation that a credible match between the proposed and experimental course of the reaction is established would seem to validate the proposed formation of bimolecular clusters.

An ionic mechanism would explain the isomerization reaction. The dissociation of  $1\text{-C}_3\text{H}_7\text{Br} \cdot \text{AlBr}_2^{\delta+} \cdot \text{AlBr}_4^{\delta-}$  and  $2\text{-C}_3\text{H}_7\text{Br} \cdot \text{AlBr}_2^{\delta+} \cdot \text{AlBr}_4^{\delta-}$  can hardly be disputed. The  $\text{AlBr}_4^-$  ion, a Lewis base, is expected to take an active part in the ionic reactions in the aprotic  $\text{CS}_2$  solvent contrary to the apparent inactivity of this ion in ionic liquids [9]. The struc-

ture of the dimeric dative covalent complex with a bromine bridge,  $1\text{-C}_3\text{H}_7\text{Br} \cdot \text{AlBr}_2 \cdot \text{Br} \cdot \text{AlBr}_3$ , facilitates the dissociation of the highly polarized complex,  $1\text{-C}_3\text{H}_7\text{Br} \cdot \text{AlBr}_2^{\delta+} \cdot \text{AlBr}_4^{\delta-}$ .

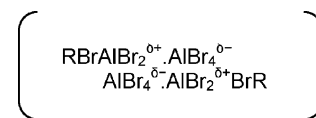
The  $\text{AlBr}_4^-$  ion does not react with 1-propyl bromide molecules. The monomeric  $\text{C}_3\text{H}_7\text{Br} \cdot \text{AlBr}_3$  complex is the least reactive component in the isomerization process followed by the dimeric  $\text{C}_3\text{H}_7\text{Br} \cdot \text{Al}_2\text{Br}_6$  complex. This indicates an increased polarization of the carbon bromine bond in the latter complex. It also indicates that steric hindrance is not a problem in these bimolecular reactions. The postulated  $[\text{C}_3\text{H}_7\text{Br} \cdot \text{Al}_2\text{Br}_6]_2$  cluster is the most reactive component according to the ratio of the reaction constants:  $k_{\text{NA}} : k_{\text{NA}_2} : k_{[\text{NA}_2]} = 1:60:1670$ . It would seem that the  $1\text{-C}_3\text{H}_7\text{Br} \cdot \text{Al}_2\text{Br}_6$  molecule is more conducive to the isomerization reaction in the cluster environment.

The absence of free carbocations in Friedel and Crafts alkylations, especially of primary reagents, indicates the occurrence of complexes or tight ion pairs of the metal halide and alkyl halide [10]. The proposed mechanism of the isomerization of 1-propyl bromide confirms this observation. The molecular orbital study of the chlorination of benzene also points to this conclusion [11].

The comparison of the calculated and experimental full course of the isomerization reaction can be considered as a confirmation of the complex reaction scheme, including the proposed dipole–dipole associated complex  $(1\text{-C}_3\text{H}_7\text{Br} \cdot \text{Al}_2\text{Br}_6)_2$ .

The result of the analysis is in good agreement with the observations and concur with literature data. The deviations of the calculated conversions from the experimental ones are small, i.e. on average 0.018 or 2.9%, columns 9 and 10 of Table 2. The similarity of the isomerization curves according to a visual inspection is satisfactory, Fig. 3.

The clusters of 1- and/or  $2\text{-C}_3\text{H}_7\text{Br} \cdot \text{Al}_2\text{Br}_6$  dipole molecules, can be visualized, particularly in apolar solvents, as:



## 4. Supplement

### 4.1. The experiments

The experiments were carried out in a specially constructed glass apparatus which facilitated a well defined start of the reaction and sample taking at specific times under dry nitrogen and at the desired reaction temperature. The reaction was stopped by discharging a small amount of the reaction mixture in a concentrated solution of sodium bromide in water at  $-20^\circ\text{C}$ . The ( $N_{\text{tot}}$ ) and ( $I_{\text{tot}}$ ) concentrations were measured by infra red analysis using calibration curves. The initial reaction rates  $V_0$  and the process data are presented in Tables 2 and 3. The concentrations were obtained

Table 2  
Starting and initial concentration of reagents, initial reaction rates and similarity factors

Exp.	$N_0$ (mol/l)	$A_{20}$ (mol/l)	[A] (mol/l)	[N] (mol/l)	$[A_2]$ (mol/l)	[NA] (mol/l)	$V_0$ ( $\times 10^5$ mol/l s)	Average (dev.)	$\Delta k/k$ (%)
B1	1.250	0.188	2.2E-06	0.972	0.049	0.278	10.40	0.013	1.8
B2	0.492	0.189	3.4E-06	0.343	0.114	0.149	5.66	0.011	1.2
B3	1.000	0.188	2.5E-06	0.753	0.064	0.247	11.90	0.010	1.4
B4	0.800	0.188	2.8E-06	0.585	0.081	0.215	8.77	0.008	1.0
B5	0.601	0.189	3.2E-06	0.426	0.101	0.175	6.77	0.006	0.6
B9	1.249	0.065	8.0E-07	1.133	0.006	0.116	0.75	0.008	4.7
C1	0.542	0.367	5.1E-06	0.327	0.258	0.215	22.10	0.013	1.6
C2	0.527	0.367	5.1E-06	0.318	0.260	0.209	21.00	0.055	6.3
C3	0.526	0.367	5.1E-06	0.317	0.260	0.209	19.50	0.021	2.4
C4	0.911	0.367	4.5E-06	0.578	0.200	0.333	50.70	0.018	2.4
C5	0.913	0.367	4.5E-06	0.579	0.200	0.334	48.40	0.007	0.9
D3	0.073	0.376	6.0E-06	0.041	0.360	0.032	0.64	0.020	2.5
D4	0.138	0.376	5.9E-06	0.078	0.346	0.060	1.89	0.049	6.7
D6	0.858	0.376	4.6E-06	0.537	0.215	0.322	53.80	0.018	2.0
E1	0.071	0.253	4.9E-06	0.043	0.239	0.027	0.46	0.016	2.9
E2	0.071	0.253	4.9E-06	0.044	0.239	0.028	0.47	0.013	2.0
E3	0.126	0.253	4.8E-06	0.078	0.229	0.048	0.97	0.030	6.8
E4	0.127	0.253	4.8E-06	0.079	0.229	0.048	0.95	0.029	10.7
E5	0.490	0.253	4.1E-06	0.320	0.168	0.170	10.20	0.036	4.4
F2	0.099	0.243	4.7E-06	0.061	0.224	0.037	0.68	0.019	4.1
F3	0.097	0.142	3.6E-06	0.067	0.126	0.031	0.38	0.020	3.7
F4	0.097	0.140	3.5E-06	0.067	0.125	0.030	0.38	0.014	2.4
H1	1.162	0.167	2.1E-06	0.915	0.044	0.247	8.42	0.010	1.6
H2	1.452	0.135	1.4E-06	1.224	0.021	0.228	4.30	0.005	1.0
H3	0.886	0.135	2.0E-06	0.701	0.042	0.185	4.66	0.005	0.9
H4	0.687	0.135	2.4E-06	0.527	0.057	0.158	3.66	0.011	2.2
H5	1.089	0.048	6.7E-07	1.002	0.004	0.087	0.42	0.008	2.9
Average								0.018	2.9

by IR-analysis using calibration curves. For a more detailed description of the experiments the author refers to a summary [2] of the original work.

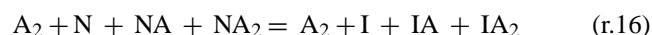
#### 4.2. Initial concentration of reagents and reaction rates<sup>2</sup>

The agents at the start of the isomerization reaction are dimeric,  $A_2$ , and monomeric aluminium bromide, A, 1-propyl bromide, N, and the monomeric complex NA. It is assumed that the dimeric complex,  $NA_2$ , is also present. They are complemented by the homologues of 2-propyl bromide as the reaction proceeds. The concentrations of N, I and NA and IA are calculated from the starting concentrations, ( $A_{20}$ ) and ( $N_0$ ) in Table 2, and from the equilibrium constants provided by [4]. Use was made of a specific program “React for Windows”, Version 1.1 for chemical reactions [12] which accommodates extended reaction mechanisms and provides the results for further calculations in spreadsheets like Excel. For  $NA_2$  and  $IA_2$  no data are available but it is assumed that their equilibrium concentrations are lower than NA respectively IA in order not to interfere with the results of [4].

<sup>2</sup> The notation of the reagents in the text is:  $AlBr_3 = A$ ,  $Al_2Br_6 = A_2$ ,  $1-C_3H_7Br = N$ ,  $2-C_3H_7Br = I$  and their complexes are NA,  $NA_2$ , IA and  $IA_2$  respectively.

#### 4.3. Analysis of the initial reaction rates as a function of the initial concentration of the reaction components

The progress of the isomerization reaction was followed by infra-red measurement of the reagent concentrations and expressed as the decrease of the total amount of N ( $N_{tot}$ ) with time for the overall reaction:



$(N_{tot})_t = (N_{free})_t + (NA)_t$  ignoring the small concentration of  $NA_2$ , and

$$(dN_{tot}/dt)_{t=0} = (dN_{free}/dt)_{t=0} + (dNA/dt)_{t=0}, \quad \text{or}$$

$$V_0 = V_{0,N_{free}} + V_{0,NA}$$

$V_{0,N_{free}}$  and  $V_{0,NA}$  are obtained from  $V_0$  in Table 3 with the ratio's  $(N_{free})/(N_{tot})$  and  $(NA)/(N_{tot})$ . The use of the subscript ‘free’ will not be continued. The notations N,  $A_2$  and (N), ( $A_2$ ) indicate the free components and the concentrations thereof.

The approach to the analysis of the data is suggested by the apparent ambiguity of two sets of initial rates for the isomerization mechanism [2] where it was mentioned that the experiments could be separated into two sets of data viz. those with  $(1-C_3H_7Br)_0 > 0.2$  mol/l and a smaller set with  $(1-C_3H_7Br)_0 < 0.2$  mol/l, conveniently indicated as  $(N_0) > (A_{20})$

Table 3  
Data of isomerization experiments B1 through H5

B1 (s)	A <sub>2</sub> : 0.188 (N <sub>t</sub> /N <sub>0</sub> )	B2 (s)	A <sub>2</sub> : 0.189 (N <sub>t</sub> /N <sub>0</sub> )	B3 (s)	A <sub>2</sub> : 0.188 (N <sub>t</sub> /N <sub>0</sub> )	B4 (s)	A <sub>2</sub> : 0.188 (N <sub>t</sub> /N <sub>0</sub> )	B5 (s)	A <sub>2</sub> : 0.189 (N <sub>t</sub> /N <sub>0</sub> )	B9 (s)	A <sub>2</sub> : 0.065 (N <sub>t</sub> /N <sub>0</sub> )	C1 (s)	A <sub>2</sub> : 0.367 (N <sub>t</sub> /N <sub>0</sub> )
735	0.936	0	0.843	320	0.965	312	0.967	350	0.961	1790	0.987	100	0.994
1272	0.887	570	0.798	705	0.909	645	0.928	675	0.924	4236	0.974	529	0.825
2130	0.834	1400	0.720	1520	0.856	1158	0.875	980	0.908	5772	0.966	912	0.698
3210	0.774	2320	0.664	2325	0.798	1800	0.815	1485	0.842	7698	0.959	1302	0.568
4752	0.700	3330	0.578	3920	0.687	2658	0.759	2115	0.782	9720	0.942	1800	0.436
7530	0.593	4548	0.499	5970	0.592	3828	0.656	3180	0.695	11820	0.934	2448	0.293
10632	0.519	6378	0.407	8298	0.503	5322	0.569	4482	0.599	14478	0.915	3372	0.162
15084	0.427	9408	0.290	10908	0.435	7590	0.469	6390	0.486	17292	0.892		
19818	0.360	12552	0.211	13440	0.374	10032	0.383	8388	0.388	19938	0.885		
27372	0.279	17568	0.122	17106	0.307	13146	0.315	10800	0.309	22680	0.872		
		21750	0.100	19848	0.262	15888	0.260	13848	0.223	25518	0.848		
						19752	0.206	16758	0.187	29082	0.842		
						23700	0.164	20826	0.135	32688	0.829		
								24018	0.086				
C2 (s)	A <sub>2</sub> : 0.367 (N <sub>t</sub> /N <sub>0</sub> )	C3 (s)	A <sub>2</sub> : 0.367 (N <sub>t</sub> /N <sub>0</sub> )	C4 (s)	A <sub>2</sub> : 0.367 (N <sub>t</sub> /N <sub>0</sub> )	C5 (s)	A <sub>2</sub> : 0.367 (N <sub>t</sub> /N <sub>0</sub> )	(s)	A <sub>2</sub> : 0.376 (N <sub>t</sub> /N <sub>0</sub> )	D4 (s)	A <sub>2</sub> : 0.376 (N <sub>t</sub> /N <sub>0</sub> )	D6 (s)	A <sub>2</sub> : 0.376 (N <sub>t</sub> /N <sub>0</sub> )
115	0.982	135	0.952	330	0.838	150	0.918	930	0.917	318	0.957	320	0.845
385	0.888	375	0.861	535	0.751	402	0.809	1824	0.838	1516	0.790	627	0.703
695	0.783	624	0.79	786	0.651	696	0.693	2826	0.764	2103	0.756	1044	0.548
1080	0.658	870	0.709	996	0.576	990	0.586	3648	0.704	2958	0.670	1308	0.460
1428	0.527	1128	0.62	1260	0.498	1218	0.519	5748	0.553	3906	0.516	1540	0.397
2160	0.338	1488	0.517	1515	0.444	1476	0.454	7212	0.460	4848	0.485	1827	0.330
2688	0.228	1776	0.427	1788	0.381	1755	0.394	8988	0.363	6000	0.378	2094	0.280
3066	0.163	2136	0.363	2052	0.317	2022	0.348	10968	0.260	7212	0.268	2400	0.232
3480	0.127	2490	0.284	2292	0.282	2358	0.288	12672	0.174			2718	0.192
		3048	0.194	2610	0.256	2610	0.263					3048	0.158
		3528	0.128			2982	0.231					3408	0.122
												3876	0.097
E1 (s)	A <sub>2</sub> : 0.253 (N <sub>t</sub> /N <sub>0</sub> )	E2 (s)	A <sub>2</sub> : 0.253 (N <sub>t</sub> /N <sub>0</sub> )	E3 (s)	A <sub>2</sub> : 0.253 (N <sub>t</sub> /N <sub>0</sub> )	E4 (s)	A <sub>2</sub> : 0.253 (N <sub>t</sub> /N <sub>0</sub> )	H1 (s)	A <sub>2</sub> : 0.167 (N <sub>t</sub> /N <sub>0</sub> )	H2 (s)	A <sub>2</sub> : 0.135 (N <sub>t</sub> /N <sub>0</sub> )	H3 (s)	A <sub>2</sub> : 0.135 (N <sub>t</sub> /N <sub>0</sub> )
1234	0.941	1220	0.931	614	0.960	624	0.954	600	0.949	600	0.972	594	0.971
2124	0.885	1821	0.900	1194	0.916	1236	0.913	1374	0.917	1200	0.949	1200	0.945
3006	0.836	2496	0.860	1800	0.871	1818	0.857	2394	0.861	2484	0.914	2394	0.893
4242	0.750	3036	0.818	2448	0.826	2406	0.841	4194	0.773	4200	0.863	4194	0.826
7236	0.607	4236	0.754	3060	0.784	3024	0.786	6000	0.712	6000	0.813	5994	0.760
9018	0.526	5700	0.692	3906	0.722	3894	0.725	8400	0.626	8520	0.746	8400	0.697
10770	0.440	7218	0.615	5130	0.645			10800	0.572	10800	0.700	10800	0.640
		9138	0.524	6378	0.559			13200	0.517	13200	0.656	13200	0.587
		11010	0.436					15600	0.470	15600	0.616	15864	0.520
		13620	0.329					18000	0.434	18366	0.567	18060	0.477
								20406	0.401				
H4 (s)	A <sub>2</sub> : 0.135 (N <sub>t</sub> /N <sub>0</sub> )	H5 (s)	A <sub>2</sub> : 0.048 (N <sub>t</sub> /N <sub>0</sub> )	E5 (s)	A <sub>2</sub> : 0.253 (N <sub>t</sub> /N <sub>0</sub> )	F2 (s)	A <sub>2</sub> : 0.243 (N <sub>t</sub> /N <sub>0</sub> )	F3 (s)	A <sub>2</sub> : 0.142 (N <sub>t</sub> /N <sub>0</sub> )	F4 (s)	A <sub>2</sub> : 0.14 (N <sub>t</sub> /N <sub>0</sub> )		
600	0.982	3120	0.988	597	0.914	648	0.968	573	0.990	1188	0.976		
1200	0.954	4860	0.987	904	0.862	1158	0.935	1176	0.972	2400	0.934		
2400	0.895	9120	0.976	1212	0.801	1824	0.887	2154	0.940	3636	0.884		
4320	0.805	12000	0.967	1542	0.733	2460	0.854	2988	0.907	4800	0.832		
6000	0.740	15000	0.945	1830	0.702	3018	0.822	4194	0.865	6000	0.787		
7800	0.670	18060	0.934	2160	0.640	3918	0.765	5358	0.820	7260	0.746		
9600	0.608			2442	0.584	4818	0.706	7536	0.746	8400	0.718		
11400	0.560			2994	0.506	5706	0.658	8534	0.677	9600	0.679		
13200	0.510			3606	0.407	6630	0.609	11694	0.608	10800	0.640		
				4290	0.326	7776	0.544	13806	0.538	13194	0.570		
				4890	0.272			16128	0.454	15654	0.497		
				5442	0.233					18120	0.415		
				6042	0.185								

Concentration of aluminium bromide (A<sub>2</sub>) in mol/l, N<sub>t</sub> ~ total conc. of 1-propyl bromide at time *t*.

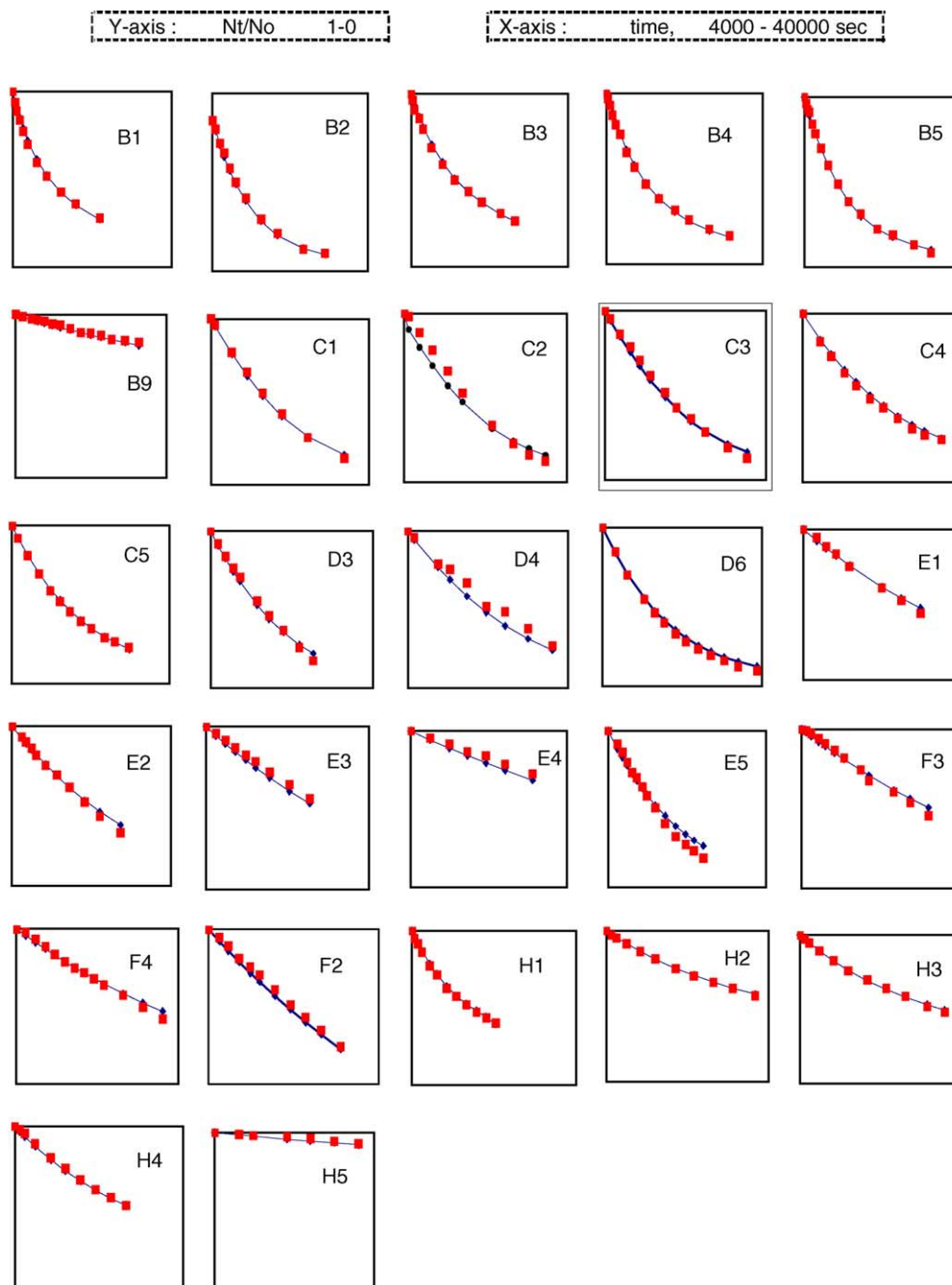


Fig. 3. Calculated isomerization curves and experimental points.

and  $(N_0) < (A_{20})$ . The two sets showed different orders of reaction.

The experiments with  $(N_0) < (A_{20})$  presented a more consistent course of reaction than the experiments with  $(N_0) > (A_{20})$  and the result of the multiple regression analysis can be expressed as follows:

$\exp(N_0) < (A_{20})$  :

$$\ln V_{0,N} = 1.05 \ln(A_2) + 1.53 \ln(N) - 6.544$$

$$\ln V_{0,NA} = 1.55 \ln(A_2) + 1.53 \ln(N) - 6.288$$

The coefficients are highly suggestive of a reaction of the 1st and 1.5 order and indicate a rate equation of:

$$\begin{aligned} V_{0,\text{calc. } N_0 < A_{20}} &\approx (A_2)(N)^{1.5} + (A_2)^{1.5}(N)^{1.5} \\ &\approx a(\text{NA})(\text{NA}_2)^{0.5} + b(\text{NA}_2)(\text{NA}_2)^{0.5} \end{aligned}$$

The  $(\text{NA}_2)^{0.5}$  term results from the dissociation of the dimeric complex  $\text{NA}_2$ .

With the coefficients  $a \sim 0.00455$  and  $b \sim 0.950$ , as mentioned in Eq. (3),  $V_0$ 's are obtained sufficiently near the

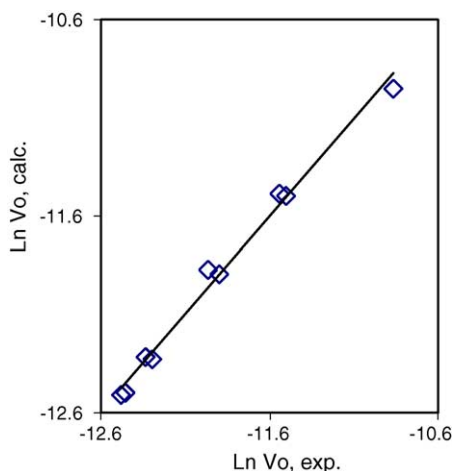


Fig. 4. Initial rates, Eq. (2). Exp. with  $N_0 < A_{20}$ .

experimental ones to attempt further analysis

$$V_{0,\text{calc. } N_0 < A_{20}} = 0.00455 \times (\text{NA})(\text{NA}_2)^{0.5} + 0.950 \times (\text{NA}_2)(\text{NA}_2)^{0.5} \quad (3)$$

The double-log or Pareto relationship between  $V_{0,\text{exp}}$  and  $V_{0,\text{calc}}$  is presented in Fig. 4 and a reaction between  $\text{AlBr}_4^-$  ions and the NA and  $\text{NA}_2$  complexes seems very likely for these experiments. This relationship, Eq. (3), is subsequently applied to all experiments and it is clear from Fig. 5 that a third term is required to describe the complete rate equation.

Assuming the Eq. (3) to resemble the  $V_0$ 's of the  $(N_0) < (A_{20})$  experiments and subtracting the calculated  $V_0$ 's for all experiments according to Eq. (3) from the experimental ones should give the residual initial rate or the third term,  $V_{0,\text{res}}$ .

Analysis of  $\ln\{V_{0,\text{res}}\}$  versus  $\ln\{A_2, N\}$  gives for the additional term:

$$\ln V_{0,\text{res}} = 2.54 \ln A_2 + 3.11 \ln N - 2.15 \text{ or } V_{0,\text{res}} \sim (A_2)^{2.54} (N)^{3.11} \sim (\text{NA})(\text{NA}_2)^2$$

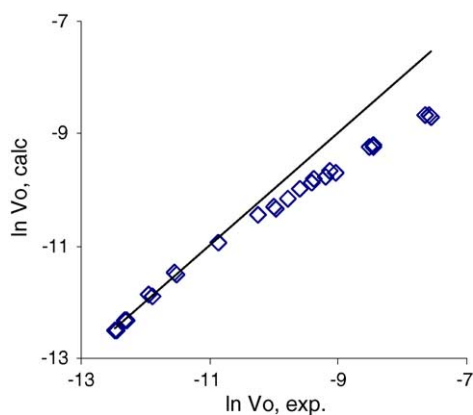


Fig. 5. Initial rates, Eq. (3). All experiments.

This expression would indicate a semi-ionic attack of highly polarized  $\text{NA}_2$  on an unsymmetrical and therefore unlikely cluster of  $[\text{NA} \cdot \text{NA}_2]$ . However, the most likely expression for  $V_{0,\text{res}}$  is  $(\text{NA}_2)^{2.5}$  and this product can be interpreted as a reaction between  $\text{A}^-$  ions and  $\text{NA}_2$  contained in dipole clusters of two molecules, reactions (r.14) and (r.15) in Table 1.

Introducing this term in Eq. (3) and carrying out a multiple regression analysis produced the following equation:

$$V_{0,\text{all}} = -d(N_{\text{tot}}/dt) = +0.0060 \times (\text{NA})(\text{NA}_2)^{0.5} + 0.359 \times (\text{NA}_2)(\text{NA}_2)^{0.5} + 1540 \times (\text{NA}_2)^2(\text{NA}_2)^{0.5}$$

The coefficients of Eq. (2) follow from those of Eq. (3) and a third coefficient such that the criteria of the analysis, an exact 1:1 relation between  $\ln V_{0,\text{exp}}$  and  $\ln V_{0,\text{calc}}$  with the intercept in the origin and a coefficient of regression close to 1.0, is complied with as is shown in Fig. 1.

A check on Eq. (2) is provided by repeating the residual procedure but now using only the first two terms of the equation. The outcome for the residual term is  $V_{0,\text{first term}} \approx (\text{A}_2)^{2.47} (\text{N})^{2.82}$  and this result is acceptably close to the proposed term of  $(\text{NA}_2)^{2.5}$ .

#### 4.4. Calculation of reaction rate constants

The reaction rate constants, mentioned in Table 1, were calculated and estimated from known data and if necessary adjusted to obtain the high similarity of the experimental and calculated reaction curves in Fig. 3.

Considering the high heat of dimerization of 13.3 kcal/mol [13] for  $\text{AlBr}_3$  the  $K_{A_2}$  value of reaction (r.1) is estimated to be of the order of  $10^{-10}$  l/mol with a fast dimerization rate of  $k_f/k_b \sim 10/10^{11}$  l/mol.

The overall  $K_{\text{NA}}$  value of 1.3 l/mol at 24 °C [4] refers to the reaction  $2 \times \text{N} + \text{A}_2 = 2 \times \text{NA}$  which is a combination of the reactions (r.1) and (r.2) of Table 1. On the assumption that a higher value applies at the lower temperature, a  $K_{\text{NA}}$  of 1.67 l/mol is obtained by calculating the best fit of  $V_{0,\text{calc}}$  with  $V_{0,\text{exp}}$  with various values of  $K_{\text{NA}}$ . For the  $K_{\text{NA}}$  of reaction (r.2) a value of  $1.29 \times 10^5$  l/mol is calculated. The complex formation is also considered to be fast compared to the isomerization reactions and the  $k_f/k_b$  ratio is set at  $1.29 \times 10^6/10$  l/mol.

The overall  $K_{\text{IA}}$  from  $2 \times \text{I} + \text{A}_2 = 2 \times \text{IA}$  is 6.8 l/mol at 24 °C [6] and for  $K_{\text{IA}}$  at -19 °C follows a value of 11.6 l/mol assuming a similar enthalpy relationship as for NA. For reaction (r.4) of Table 1 a  $K_{\text{IA}}$  value of  $3.4 \times 10^5$  l/mol is calculated.

The  $K_{\text{NA}_2}$  value is set at 15 000/10 l/mol in order not to interfere with the observations reported in [4]. For this value a best fit procedure as for  $K_{\text{NA}}$  was followed and the  $\text{NA}_2$  concentration is on average 5% of the NA concentration. A higher value for  $K_{\text{IA}_2}$  in reaction (r.5) in Table 1 is to be expected and it is set at 17 000/10 l/mol in the final isomerization scheme.



To obtain the initial concentrations of the reactions (r.1)–(r.3), the rate data and the starting concentrations are introduced into the Mechanistic Data section of the REACT program and the reaction times into the appropriate Reaction Times section [12]. For the initial concentrations of Table 3 a reaction time of 1 s is sufficient to reach a stable state.

#### 4.5. The isomerization scheme

The isomerization scheme for the calculation of the reaction curves according to Eq. (2) is presented in Table 1.

The rate constants of reactions (r.6)–(r.10) are arbitrarily chosen. The reaction (r.8) is included to facilitate an isomerization equilibrium, of about 1% 1-C<sub>3</sub>H<sub>7</sub>Br [14].

The rates of reactions (r.6)–(r.8) do not interfere with the observations of [4], they provide adequate cluster concentration and rapidly establish equilibrium states. The differentiation of the *K*-values for N<sub>2</sub>A<sub>4</sub>, NIA<sub>4</sub> and I<sub>2</sub>A<sub>4</sub> result from adjustments to the calculated curves of the experiments with the highest initial concentrations and are in line with the expected individual dipole moments. The dissociation of NA<sub>2</sub> and IA<sub>2</sub> is in accordance with acceptable ionic concentrations and isomerization curves.

It is assumed that the ionic molecule, Al<sub>2</sub>Br<sub>7</sub><sup>−</sup>, which is a product of the displacement reactions (r.12)–(r.15), rapidly dissociates into AlBr<sub>3</sub> and AlBr<sub>4</sub><sup>−</sup> in the aprotic environment of CS<sub>2</sub> as opposed to the more stabilizing environment of an ionic liquid [9].

The rate constants of reactions (r.11a), (r.12a) and (r.13) follow from the coefficients of Eq. (2) which are a product of these constants and the relevant equilibrium constants. The rate constant of reaction (r.14a) reflects the higher reactivity of NA<sub>2</sub> in the cluster formation.

It will be clear from these calculations that experimentally determined *K*-values might change the rate constants, however, the calculated curves will remain as presented in Fig. 3.

#### 4.6. Similarity of reaction curves

The search for the correct reaction mechanism involves a visual comparison of the calculated curves with the experimental observations. An efficient method for comparing the results of different reaction mechanisms is to calculate the average deviation of the absolute differences of the calculated and the experimental observations.

In order to compare individual experiments the average deviation is divided by  $(1 - (N_t/N_0)_{\text{final}})$  which is indicated as  $\Delta k/k$  in Table 2. This factor is assumed to be largely independent of the extent of the reaction.

#### References

- [1] M.B. Smith, J. March, March's Advanced Organic Chemistry, 5th ed., Wiley–Interscience, New York, 2000, p. 1394.
- [2] H.S.A. Douwes, E.C. Kooyman, Rec. Trav. Chim. 83 (1964) 276.
- [3] Sang Up Choi, et al., Bull. Korean Chem. Soc. 3 (2) (1982) 55;  
Sang Up Choi, et al., Bull. Korean Chem. Soc. 3 (4) (1982) 144;  
Sang Up Choi, et al., Bull. Korean Chem. Soc. 6 (3) (1985) 124.
- [4] E.H. Adema, et al., Rec. Trav. Chim. 85 (1966) 377.
- [5] A.A. Malkov, et al., Polyhedron 16 (23) (1997) 4081.
- [6] H.S.A. Douwes, Unpublished results from the thesis, University of Amsterdam, 1962.
- [7] E.H. Adema, F.L. Sixma, Rec. Trav. Chim. 81 (1962) 323.
- [8] Oh Cheun Kwun, et al., Bull. Korean Chem. Soc. 2 (3) (1981).
- [9] Li Xiao, et al., J. Mol. Catal. A: Chem. 214 (2004) 121.
- [10] M.B. Smith, J. March, March's Advanced Organic Chemistry, 5th ed., Wiley–Interscience, New York, 2000, p. 711.
- [11] Yoshihiro Osamura, et al., J. Mol. Catal.: Theochem. 461/462 (1999) 399–416.
- [12] REACT for Windows 1.2, Alchemy Software, Wesley Chapel, FL, USA, 2000.
- [13] E.N. Guryana, I.P. Goldstein, Donor–Acceptor Bond, Wiley–Interscience, New York, 1975, p. 69.
- [14] W. Garrard, et al., J. Chem. Soc. (1964) 2314.