

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

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Abstract

The kinetics of the aluminium bromide catalyzed isomerization of 1-propyl bromide corresponds to a nucleophilic displacement of the aliphatic bromine contained in the monomeric and dimeric complexes of the alkyl bromide with aluminium bromide, $(1\text{-C}_3\text{H}_7\text{BrAlBr}_3)$ and $(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)$, and the antiparallel dipole pair of the dimeric complexes. The initial rate analysis of the isomerization process shows that parallel mixed dipole pairs of the monomeric and dimeric complexes, $(1\text{-C}_3\text{H}_7\text{Br}\cdot\text{AlBr}_2^{\delta+}\text{AlBr}_4^{\delta-})\cdot(1\text{-C}_3\text{H}_7^{\Delta+}\text{Br}\cdot\text{AlBr}_3^{\Delta-})$ and $(1\text{-C}_3\text{H}_7^{\Delta+}\text{Br}\cdot\text{AlBr}_3^{\Delta-})\cdot(1\text{-C}_3\text{H}_7\text{Br}\cdot\text{AlBr}_2^{\delta+}\text{AlBr}_4^{\delta-})$, could also take part in the isomerization process. The kinetics of the process is investigated and the conclusion is that the isomerization does not require the mixed parallel dipole pairs for the reaction.

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1. Introduction

The review “The Story of the Wagner–Meerwein rearrangement” [1] concluded with the statement that “Meerwein’s hypothesis of carbocations as intermediates [2] was one of the conceptually great breakthroughs in physical organic chemistry”. Hence, the typical description of the aluminium bromide catalyzed isomerization of 1-propyl bromide as a Wagner–Meerwein rearrangement of the carbocation [3]. Whereas carbocations are often involved in rearrangement reactions [4], the investigation of the isomerization reaction of 1-propyl bromide to the secondary compound revealed a nucleophilic substitution of the aliphatic bromide by the aluminium bromide ion AlBr_4^- [5]. The substitution is accompanied by a rate determining 2,1 hydride shift [6].

In the previous paper on the rearrangement of 1-propyl bromide [5], it was demonstrated that the aliphatic bromide is contained in complexes with monomeric and dimeric aluminium bromide, $1\text{-C}_3\text{H}_7\text{BrAlBr}_3$ and $1\text{-C}_3\text{H}_7\text{Al}_2\text{Br}_6$. The multiple linear regression analyses of the initial reaction rates showed that

the highly polarized dimeric complex also takes part in the isomerization reaction as an antiparallel dipole pair, Fig. 1.

The object of this paper is to investigate the formation of a mixed dipole pair consisting of monomeric and dimeric complexes $(1\text{-C}_3\text{H}_7^{\delta+}\text{BrAl}_2\text{Br}_6^{\delta-})\cdot(1\text{-C}_3\text{H}_7^{\Delta+}\text{BrAlBr}_3^{\Delta-})$ in parallel configuration and observe its effect on the kinetics and the full course of the isomerization reaction.

The results are discussed in the Section 2. The method of analysis, the formation of the reaction scheme and the calculations for the conversion are described in the Section 4.

2. Results and discussion

2.1. Results

The formation of parallel dipole pairs results in a considerable increase of the overall dipole moment [7]. The 1-propyl bromide of the monomeric complex in the front position of a parallel pair is expected to be strongly polarized by the dipole of the dimeric compound in the rear position due to the high polarizability of bromine. The reactivities of the 1-propyl bromide molecules in the monomeric and dimeric complexes in the front position of the mixed dipole pairs become comparable.

The incorporation of mixed dipole pairs in the multiple regression analysis of the initial reaction rates and the com-

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Table 1
Reaction rates of mixed complexes of the dipole pairs of 1- and 2-propyl bromide

		l/mol s
$(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)\cdot(1\text{-C}_3\text{H}_7\text{BrAlBr}_3) + (1\text{-C}_3\text{H}_7\text{BrAlBr}_3)\cdot(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)$	$k_1 + k_2$	136
$(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)\cdot(2\text{-C}_3\text{H}_7\text{BrAlBr}_3) + (2\text{-C}_3\text{H}_7\text{BrAlBr}_3)\cdot(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)$	k_3	34
$(1\text{-C}_3\text{H}_7\text{BrAlBr}_3)\cdot(2\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6) + (2\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)\cdot(1\text{-C}_3\text{H}_7\text{BrAlBr}_3)$	k_4	34

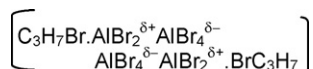


Fig. 1. Antiparallel dipole pair of the dimeric complex.

parison of the calculated and experimental conversion data demonstrated that the mixed dipole pairs of $1\text{-C}_3\text{H}_7\text{BrAlBr}_3$ and $1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6$ could take part in the isomerization process, Section 4.2. For the dipole pairs with the 1-propyl bromide complexes, $(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)\cdot(1\text{-C}_3\text{H}_7\text{BrAlBr}_3)$ and $(1\text{-C}_3\text{H}_7\text{BrAlBr}_3)\cdot(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)$, an overall reaction rate of 136 l/mol s was determined, Table 1, Section 2.2.

It follows that a reaction rate of 68 l/mol s could be allocated to each set of mixed dipole pairs containing 1-propyl bromide and its isomerization product 2-propyl bromide and their complexes: $(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)\cdot(2\text{-C}_3\text{H}_7\text{BrAlBr}_3) + (2\text{-C}_3\text{H}_7\text{BrAlBr}_3)\cdot(1\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)$ and $(1\text{-C}_3\text{H}_7\text{BrAlBr}_3)\cdot(2\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6) + (2\text{-C}_3\text{H}_7\text{BrAl}_2\text{Br}_6)\cdot(1\text{-C}_3\text{H}_7\text{BrAlBr}_3)$, Table 1 Section 2.2.

2.2. Discussion

The investigation by Ghanadzadeh Gilani et al. [7] of the aggregation of benzaldehydes and acetone derivatives in non-polar solvents demonstrated the existence of antiparallel and parallel dipole pairs of compounds with a high dipole moment in a nonpolar environment. These findings provide considerable support to the proposed antiparallel dipole pairs of the dimeric complexes, Fig. 1, in the aluminium bromide catalyzed isomerization of 1-propyl bromide [5]. The evidence of dipole pairs of different acetone derivatives in a parallel or head-to-tail configuration [7] indicates that the presence of mixed dipole pairs of dimeric and monomeric complexes, Fig. 2, in the isomerization scheme is possible and should be investigated. The multi regression analysis and subsequent calculations, Section 4.2, have shown that mixed dipole pairs can take part in the isomerization process.

Three sets of configurations of mixed pairs have to be considered, Table 1. The first set contains only 1-propyl bromide complexes and the other two sets contain the 2-propyl bromide and its complexes. A distinction between the parallel configurations within the three sets is not possible.

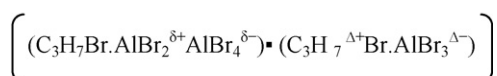


Fig. 2. Parallel or head-to-tail dipole complex of the mixed dipole pair.

The initial rate analysis and conversion calculations, Section 4.2, resulted in the reactivity data of the three sets of mixed parallel configurations in Table 1.

The reactivities of both 1-propyl bromide monomeric and dimeric complexes in the front position of the mixed dipole are expected to be of the order of 68 l/mol s. However, the sum of the reaction rates k_3 and k_4 never exceeds 68 l/mol s and the best match for the calculated and experimental data was obtained with a rate of 34 l/mol s for k_3 and for k_4 .

2.2.1. Mixed dipole pairs in parallel configuration.

A possible mechanism that satisfies the reaction rates in Table 1 is a nucleophilic substitution by the (AlBr_4^-) ion of the 1-propyl bromide in the first or front position of the dipole pairs with a simultaneous isomerization of the 1-propyl bromide component in the second or rear position. The polarization of the 1-propyl group in the rear position enhances its reactivity sufficiently for a rearrangement reaction.

The rearrangement of the front alkyl group by (AlBr_4^-) produces the nucleophilic¹ $(\text{Al}_2\text{Br}_7^-)$ or (AlBr_4^-) ions in close proximity of the 1-propyl bromide in the second or rear position resulting in an isomerization of the highly polarized 1-propyl bromide in this position. If $k_1 = k_2 = 68$ l/mol s, it follows that $k_3 = k_4 = 34$ l/mol s. It is a condition of this option that every reaction of the front component must be followed by a rearrangement of the rear compound. The likelihood of the suggested simultaneous or subsequent reaction is not great, it would only provide an unusual explanation of the isomerization process. Full courses of the simultaneous or subsequent reaction are calculated and the conversions match the experimental data with an average deviation of 3.4%, Table 3.

2.2.2. Mixed dipole pairs in antiparallel configuration.

The equal reaction rates of the mixed dipole complexes are suggestive of a single intermediate compound for the reaction. The antiparallel dipole–dipole complex could be such an intermediate in which the 1-propyl bromide and 2-propyl bromide rapidly interchange. Such an intermediate is speculative but might involve a rearrangement of the dative bonds between the propyl bromides and the aluminium bromide of the complexes in Fig. 3. The reaction of Eq. (1) is incorporated in the kinetics

¹ The $(\text{Al}_2\text{Br}_7^-)$ ion is a Lewis acid in the inert environment of carbon disulfide.

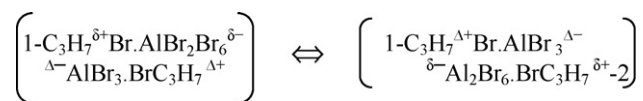
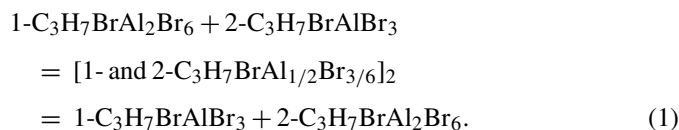


Fig. 3. Interchange of mixed propyl bromide complexes in antiparallel configuration.

of the process by an identical product from the two reactions²:



The major difference between this process option and the simultaneous mechanism is the concentration of the mixed dipole–dipole complexes. The concentration of these complexes in the simultaneous reaction is twice that in the reaction with the antiparallel intermediate. Due to this difference a better result of 2.7% is calculated for the average difference of the experimental and calculated conversions in the full courses of the reactions with the antiparallel intermediate according to Table 2.

2.2.3. Dipole pairs of dimeric complexes in antiparallel configuration

The result of the full courses of reactions with the mixed dipole pairs does not compare favorably with the isomerization process without the mixed complex pairs, Table 3. The deviations for the process with the parallel mixed dipole complexes, 3.4%, occurred in nearly all reactions. The deviations of the reactions with the antiparallel mixed complexes, 2.7%, were all observed in reactions with a high concentration of 1-propyl bromide and aluminium bromide showing a higher rate of reaction after 30–60% conversion. For the reactions with the dipole pairs of the dimeric complexes only, Fig. 1, an average deviation of 1.4% was obtained [5]³.

3. Conclusion

The analysis of the initial rates of reaction has shown that mixed dipole complexes of 1-C₃H₇BrAlBr₃ and 1-C₃H₇BrAl₂Br₆ could take part in the aluminium bromide catalyzed isomerization of 1-propyl bromide together with the dipole pairs of the dimeric complexes. This is not surprising as the ratio of the dimeric dipole pairs and the mixed dipole pairs is determined by the concentration of aluminium bromide only. The participation of the dimeric dipole pair was demonstrated earlier [5].

The suggestion of the mixed dipole pairs in parallel and antiparallel configurations in the kinetics of the reaction leads as yet to unlikely reaction mechanisms and less-satisfactory results for the calculated full courses of the isomerization process. The preferred mechanism of the isomerization reaction remains a nucleophilic displacement of the aliphatic bromine contained in

the monomeric and dimeric complexes with aluminium bromide and in the antiparallel dipole pairs of the dimeric complexes with aluminium bromide [5].

This investigation shows that a kinetic expression, Eq. (2), is often not sufficient evidence for the establishment of a reaction mechanism. The data of full courses of reaction may be required to explain the reaction mechanism particularly for complicated processes, [5,9–12].

The conclusion is that the carbocation CH₃CH₂CH₂⁺ is not an intermediate in the aluminium bromide catalyzed rearrangement of 1-propyl bromide. It is suggested that the aluminium bromide catalyzed isomerization of 1-propyl bromide is not used for the illustration of a Wagner–Meerwein rearrangement [3].

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 °C. The propyl bromide concentrations were obtained by IR-analysis using calibration curves. For a more detailed description of the experiments the author refers to [6].

4.2. Initial rate equation

The incorporation of mixed dipole pairs in the multiple regression analysis of the initial reaction rates as presented in the reaction scheme of Table 2 resulted in the following (simplified) initial rate equation for the monomeric complex 1-C₃H₇Br·AlBr₃, (NA), and the dimeric complex 1-C₃H₇Br·Al₂Br₆, (NA₂). 1-Propyl bromide is indicated by (N).

$$\begin{aligned} (-d(N)/dt)_{t=0} = 0.0048 \times (NA)(NA_2)^{0.5} + 0.522 \times (NA_2)^{1.5} \\ + 6.8 \times (NA)(NA_2)^{1.5} + 410 \times (NA_2)^{2.5} \end{aligned} \quad (2)$$

The square root terms are the expressions of the dissociation of the dimeric complex, NA₂, leading to the AlBr₄[–] ion (A[–]). The first and second terms refer to the isomerization of 1-propyl bromide in the monomeric (NA) and dimeric complexes (NA₂). The third term belongs to the mixed dipole pairs in a linear or head-to-tail configuration, (NA₂)·(NA) or (NA)·(NA₂), Fig. 2, or the antiparallel configuration as presented in Fig. 3. The fourth term relates to the antiparallel dipole pairs of the dimeric complexes of Fig. 3.

The relation of the experimental and calculated initial rates according to Eq. (2) is shown in Fig. 4 which is a plot of $\ln V_{0,\text{exp}} = 1.0001 \times \ln V_{0,\text{calc}} - 0.00052$. This shows that mixed dipole pairs can participate in the isomerization reaction. The $V_{0,\text{calc}}$ is obtained from Eq. (2), the initial concentrations of the reagents, Table 3 and the appropriate complex equilibria.

The equilibrium constant for the mixed pairs (NA₂)·(NA) and (NA)·(NA₂), is taken as $K_{\text{NA}_2\text{A}_3} = 5 \text{ l/mol}$ which constant is

² [1- and 2-C₃H₇BrAl_{1/2}Br_{3/6}]₂ is an expression of the mixed antiparallel dipole pair in which the interchange occurs, Eq. (1).

³ Minor corrections were applied in the reaction scheme of [5].

Table 2

Reaction scheme of the isomerization of 1-C₃H₇Br in the presence of Al₂Br₆

Complex and cluster formation:	<i>k_f/k_b</i>
Reactions:	
1-C ₃ H ₇ Br + AlBr ₃ = 1-C ₃ H ₇ Br·AlBr ₃	1.29 × 10 ⁶ /10 l/mole
1-C ₃ H ₇ BrAlBr ₃ + AlBr ₃ = 1-C ₃ H ₇ Br·Al ₂ Br ₆	15000/10 l/mole
2-C ₃ H ₇ Br + AlBr ₃ = 2-C ₃ H ₇ Br·AlBr ₃	3.4 × 10 ⁶ /10 l/mole
2-C ₃ H ₇ Br·AlBr ₃ + AlBr ₃ = 2-C ₃ H ₇ Br·Al ₂ Br ₆	17000/10 l/mole
1-C ₃ H ₇ Br·AlBr ₃ + 1-C ₃ H ₇ Br·Al ₂ Br ₆ = [1-C ₃ H ₇ BrAl _{1/2} Br _{3/6}] ₂	1000/200 l/mole
1-C ₃ H ₇ Br·AlBr ₃ + 2-C ₃ H ₇ Br·Al ₂ Br ₆ = [1-and2-C ₃ H ₇ BrAl _{1/2} Br _{3/6}] ₂	1000/200 l/mole
2-C ₃ H ₇ Br·AlBr ₃ + 1-C ₃ H ₇ Br·Al ₂ Br ₆ = [1-and2-C ₃ H ₇ BrAl _{1/2} Br _{3/6}] ₂	1000/200 l/mole
2-C ₃ H ₇ Br·AlBr ₃ + 2-C ₃ H ₇ Br·Al ₂ Br ₆ = [2-C ₃ H ₇ BrAl _{1/2} Br _{3/6}] ₂	1100/200 l/mole
1-C ₃ H ₇ Br·Al ₂ Br ₆ + 1-C ₃ H ₇ Br·Al ₂ Br ₆ = [1-C ₃ H ₇ Br·Al ₂ Br ₆] ₂	1000/10 l/mole
1-C ₃ H ₇ Br·Al ₂ Br ₆ + 2-C ₃ H ₇ Br·Al ₂ Br ₆ = [1-and2-C ₃ H ₇ Br·Al ₂ Br ₆] ₂	1000/10 l/mole
2-C ₃ H ₇ Br·Al ₂ Br ₆ + 2-C ₃ H ₇ Br·Al ₂ Br ₆ = [2-C ₃ H ₇ Br·Al ₂ Br ₆] ₂	1100/10 l/mole
Dissociation:	
Al ₂ Br ₆ = AlBr ₃ + AlBr ₃	10/10 ¹¹ mole/l
1-C ₃ H ₇ Br·Al ₂ Br ₆ = 1-C ₃ H ₇ BrAlBr ₂ ⁺ + AlBr ₄ ⁻	10/10 ⁵ mole/l
2-C ₃ H ₇ Br·Al ₂ Br ₆ = 2-C ₃ H ₇ BrAlBr ₂ ⁺ + AlBr ₄ ⁻	11/10 ⁵ mole/l
Isomerization ^a :	
AlBr ₄ ⁻ + 1-C ₃ H ₇ BrAlBr ₃ = 2-C ₃ H ₇ BrAlBr ₃ + AlBr ₄ ⁻	0.48 l/mol s
AlBr ₄ ⁻ + 1-C ₃ H ₇ BrAl ₂ Br ₆ = 2-C ₃ H ₇ BrAlBr ₃ + AlBr ₃ + AlBr ₄ ⁻	52.2 l/mol s
AlBr ₄ ⁻ + [1-C ₃ H ₇ BrAl _{1/2} Br _{3/6}] ₂ = 2-C ₃ H ₇ BrAlBr ₃ + 1-C ₃ H ₇ BrAl ₂ Br ₆ + AlBr ₄ ⁻	136 l/mol s
AlBr ₄ ⁻ + [1-and 2-C ₃ H ₇ BrAl _{1/2} Br _{3/6}] ₂ = 2-C ₃ H ₇ BrAlBr ₃ + 2-C ₃ H ₇ BrAl ₂ Br ₆ + AlBr ₄ ⁻	68 l/mol s
AlBr ₄ ⁻ + [1-C ₃ H ₇ BrAl ₂ Br ₆] ₂ = 2-C ₃ H ₇ BrAlBr ₃ + 1-C ₃ H ₇ BrAl ₂ Br ₆ + AlBr ₃ + AlBr ₄ ⁻	410 l/mol s
AlBr ₄ ⁻ + [1-and 2-C ₃ H ₇ BrAl ₂ Br ₆] ₂ = 2-C ₃ H ₇ BrAlBr ₃ + 2-C ₃ H ₇ BrAl ₂ Br ₆ + AlBr ₃ + AlBr ₄ ⁻	230 l/mol s

^a [1- and 2-C₃H₇BrAl_{1/2}Br_{3/6}]₂ is an expression of the mixed antiparallel dipole pair in which the interchange occurs, Eq. (1). The return reactions were based on a 98% equilibrium.

Table 3

Initial concentration of reagents, initial reaction rates and average difference of experimental and calculated conversion data

Exp.	Initial conc. 1-C ₃ H ₇ Br mole/l	Initial conc. Al ₂ Br ₆ mole/l	Initial rate of reaction × 10 ⁵ mole/l	Interchange reaction Aver. Diff.	Simultaneous reaction Aver. Diff.	Dimeric pairs only Aver. Diff.
B1	1.250	0.188	10.40	0.004	0.043	0.009
B2	0.492	0.189	5.66	0.010	0.026	0.010
B3	1.000	0.188	11.90	0.008	0.044	0.010
B4	0.800	0.188	8.77	0.005	0.042	0.008
B5	0.601	0.189	6.77	0.007	0.037	0.006
B9	1.249	0.065	0.75	0.005	0.013	0.006
C1	0.542	0.367	22.10	0.047	0.049	0.013
C2	0.527	0.367	21.00	0.068	0.078	0.055
C3	0.526	0.367	19.50	0.053	0.043	0.024
C4	0.911	0.367	50.70	0.058	0.027	0.012
C5	0.913	0.367	48.40	0.049	0.021	0.010
D3	0.073	0.376	0.64	0.027	0.026	0.019
D4	0.138	0.376	1.89	0.021	0.042	0.040
D6	0.858	0.376	53.80	0.080	0.040	0.009
E1	0.071	0.253	0.46	0.024	0.028	0.012
E2	0.071	0.253	0.47	0.026	0.054	0.011
E3	0.126	0.253	0.97	0.013	0.015	0.023
E4	0.127	0.253	0.95	0.015	0.015	0.029
E5	0.490	0.253	10.20	0.059	0.015	0.023
F2	0.099	0.243	0.68	0.009	0.015	0.017
F3	0.097	0.142	0.38	0.023	0.039	0.018
F4	0.097	0.140	0.38	0.015	0.053	0.011
H1	1.162	0.167	8.42	0.011	0.050	0.008
H2	1.452	0.135	4.30	0.036	0.011	0.004
H3	0.886	0.135	4.66	0.013	0.030	0.009
H4	0.687	0.135	3.66	0.016	0.053	0.011
H5	1.089	0.048	0.42	0.009	0.012	0.013
			Average difference:	0.027	0.035	0.014
			Standard deviation:	0.016	0.016	0.006

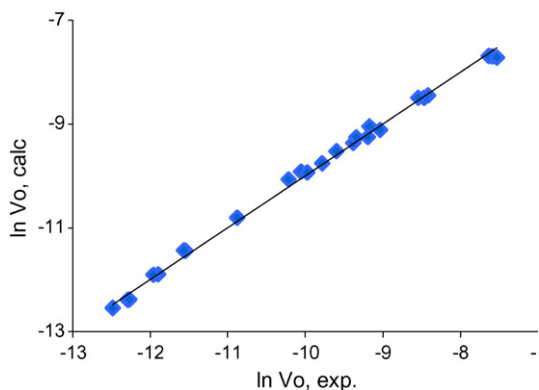


Fig. 4. Experimental vs. calculated initial rates. Table 1.

assumed to be 20 times smaller than for the antiparallel pairs, $K_{N2A3} = 100$ l/mol. The dissociation constant of NA_2 into (NA^+) and (A^-) is $K_{ion} = 10^{-4}$ l/mol. These data are used in the conversion of the third term of the initial rate equation into the kinetic equation:

$$\begin{aligned}
 &6.8 \times (NA)(NA_2)^{1.5} \\
 &= k_1 \times (NA_2) \cdot (NA) \times (A^-) + k_2 \times (NA) \cdot (NA_2) \times (A^-) \\
 &= (k_1 K_{N2A3} + k_2 K_{N2A3})(NA)(NA_2)(K_{ion} \cdot NA_2)^{0.5} \quad (3)
 \end{aligned}$$

or

$$(k_1 + k_2) = 1361/\text{mol s} \quad (4)$$

The reaction rates of the mixed dipole pairs of Table 1 and the conversion of the remaining terms of Eq. (2) into their kinetic expressions, Table 2, provided the reaction scheme⁴ for a comparison of the calculated conversions with the experimental data. The [1- and 2- $C_3H_7BrAl_{1/2}Br_{3/6}$]₂ compound is indicative for the intermediate complex resulting from the rapid interchange of the antiparallel dipole–dipole complexes as presented in Fig. 3.

The rate constants of Table 2 follow from the coefficients of Eq. (2) which are themselves a product of these rate constants and the relevant equilibrium constants. It will be clear from these calculations that the assumed equilibrium values will change the rate constants of Table 2. However, this does not affect the comparison of the calculated conversions and the experimental results.

The initial concentration of the reactants and the average difference experimental and calculated conversion are presented in Table 3.

The reaction scheme of Table 2 is used for the calculation of the full courses of reaction with the appropriate modifications for the parallel and antiparallel configurations.

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⁴ The conversion data were obtained with the REACT program [8] using the reactions of Table 2.

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