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Ionic Bromination of Ethane and Other Alkanes (Cycloalkanes) with Bromine Catalyzed by the Polyhalomethane•2AlBr₃ Aprotic Organic Superacids under Mild Conditions

Irena S. Akhrem*, Alexander V. Orlinkov, Lyudmila V. Afanas'eva, Evgenii I. Mysov and Mark E. Vol'pin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 117813, Russia

Abstract: *The polyhalomethane•2AlBr$_3$ aprotic organic superacids were shown to effectively catalyze low-temperature ionic bromination of (cyclo)alkanes. Ethane readily reacts with Br$_2$ at 55-65^0, affording mainly 1,2-dibromoethane. Propane, butane, and C$_5$-C$_6$ cycloalkanes react at -40^0÷ -20^0, resulting in monobromides with high yields and good selectivity.*

Ionic bromination of alkanes and cycloalkanes with Br$_2$ was first reported in 1973 by Olah et al.[1] However, the activity of AgSbF$_6$ as a Lewis acid was very low: the reaction was not acceptable for linear alkanes, the yields of monobromides for simple cycloalkanes amounted to 5-27% on the catalyst, while the isoalkane reactions were not selective and accompanied by polybromination. Ionic bromination of isoalkanes in HSO$_3$F-SbF$_5$ media also led to low yields of monobromides alongside polybromides and fragmentation products.[2] The aprotic organic superacids RCOX•2AlBr$_3$[3] were shown to effectively catalyze ionic monobromination of C$_4$-C$_7$ n-alkanes and C$_5$-C$_6$ cycloalkanes.[4] The formation of carbonyl-containing compounds as the by-products was the main shortcoming of the RCOX• 2AlBr$_3$ catalysts. Recently we have shown that polyhalomethanes in combination with AlBr$_3$ display the properties of aprotic organic superacids, initiating various reactions of alkanes and cycloalkanes.[5-7] We now report our results on effective liquid-phase ionic bromination of alkanes and cycloalkanes including ethane heretofore unreactive toward Br$_2$ under mild conditions.

Ethane effectively reacts with Br$_2$ in the presence of CBr$_4$•2AlBr$_3$ both in CH$_2$Br$_2$ solution and under solvent-free conditions[8] at 55-65^0, affording 1, 2-dibromoethane as the main product alonside a small amount of ethyl bromide:

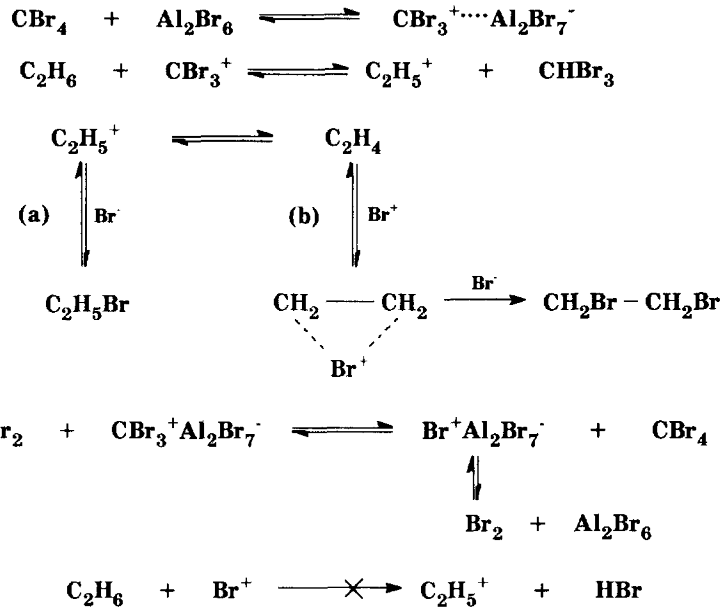
$$\mathbf{C_2H_6 + Br_2 + CBr_4{\bullet}2AlBr_3 \xrightarrow[55\text{-}65^0]{} 1,2\text{-}C_2H_4Br_2 + CHBr_3{\bullet}2AlBr_3 + HBr}$$

In a stoichiometric reaction without solvent, Br$_2$ is consumed completely over 18h, and the total yield of brominated products is 100% on the initial Br$_2$. This shows that formally both bromine atoms of the Br$_2$ molecule are involved in brominated products.[9] Under similar conditions for 6h, the same products are formed, with the total yield of 84% on Br$_2$. Increasing the [Br$_2$]: [CBr$_4$•2AlBr$_3$] ratio reduces the effectivity of bromination: when this ratio equals 4, the yield falls down to 26% on Br$_2$. The maximum yield of brominated products does not exceed 1.5 mol per 1 mol of CBr_4. Qualitatively the reaction in CH_2Br_2 solution proceeds analogously. Bromination of ethane under the action of $CBr_4{\bullet}2AlBr_3$ also occurs in the absence of Br_2.[10] Yet in this case, only the monobrominated product C_2H_5Br is formed, its yield being 60% on CBr_4 for 6h. On the contrary, Br_2 in the presence of $AlBr_3$ does not react with ethane under similar conditions.

It is noteworthy that ethane bromination by Br_2 in the presence of $CBr_4{\bullet}2AlBr_3$ can also be achieved at atmospheric pressure of ethane. In this case, C_2H_5Br, 1, 2-$C_2H_4Br_2$, and 1, 1, 2, 2, -$C_2H_2Br_4$ (in molar ratio ca. 1: 3: 5) are formed, with the total yield of 73% on Br_2 for 3h.

The above results may be interpreted by Scheme 1.

Scheme 1



According to this scheme, the CBr_3^+ cation abstracts hydride ion from ethane to form ethyl cation and CBr_3H.Ethyl cation adds Br^- from the $Al_2Br_7^-$ anion or the Br_2 molecule, affording EtBr (and Al_2Br_6 or Br^+, respectively). The pathway **(a)** seems to be the only direction in the absence of Br_2, while in the presence of Br_2 the pathway **(b)** becomes the predominant one. Since $Br^+Al_2Br_7$ does not react with ethane under the studied conditions, the reaction is not catalytic. Moreover, increasing the $[Br_2]$: $[CBr_4{\bullet}2AlBr_3]$ ratio leads to the lessening of the system's activity, lowering the content of the CBr_3^+ cation in the reaction medium.

The essential difference in the composition of brominated products in reactions at atmospheric and higher pressures may be explained by a low stationary ethane concentration in the first case. For this reason, further bromination of the initially formed $C_2H_4Br_2$ becomes a pronounced tendency at atmospheric pressure.

At room temperature ethane bromination does not occur. On the contrary, a more active propane readily reacts with Br_2 even at -20^0 with selective formation of i-PrBr:

$$C_3H_8 + Br_2 \xrightarrow[\mathbf{-20^0,\ 3h}]{CBr_4{\bullet}2AlBr_3} \mathbf{i\text{-}PrBr} + \mathbf{HBr}$$

48% on Br_2[11] (96% on CBr_4)

At -10^0 or 0^0 propane is fully brominated. With the increase of temperature, however, dibromide is also formed, and the ratio [PrBr]: [C3H6Br2] decreases to 6: 1 (-10^0, 3h) and 2: 1 (0^0, 2h). At 0^0 bromination becomes non-selective.

n-Butane is completely brominated at -20^0 for 2h, with selective formation of monobromides representing the mixture of three isomers: [t-BuBr]: [i-BuBr+sec-BuBr]=1: 0.4.

$$\mathbf{C_4H_{10} + Br_2 \xrightarrow[-20^0,\ 2h]{CBr_4{\bullet}2AlBr_3} Me_3CBr_3 + Me(Et)CHBr + Me_2CHCH_2Br + HBr}$$

Overall yield: 105% on Br_2 (425% on CBr_4)

In this reaction $CCl_4{\bullet}2AlBr_3$ is markedly less active: the yield of butylbromides is decreased to 13%.

Bromination of cyclopentane, cyclohexane, and methylcyclopentane proceeds noticeably at -40^0 and effectively and selectively at -20^0. The yields of monobromides reach 76% on Br_2 and 600% on Cat. Polybromination products are absent or formed only as traces. Reaction of cyclopentane leads only to cyclopenthylbromide. Both cyclohexane and methylcyclopentane at -40^0 and -20^0 afford a single and the same product, *viz.* cyclohexylbromide. This result can be explained by the instability of 1-bromo-1-methyl-cyclopentane (initially formed from both cycloalkanes) which irreversibly transforms into a more stable secondary cyclohexylbromide.

The order of catalyst activity for cyclohexane bromination at -20^0 is as follows (the yields of cyclo-$C_6H_{11}Br$ on Br_2 are given for [cyclo-C_6H_{12}]: [Br_2]: [Cat]=10: 4: 1):

$$\begin{array}{ccccccccc}
\mathbf{CBr_4{\bullet}2AlBr_3} & > & \mathbf{CHBr_3{\bullet}2AlBr_3} & > & \mathbf{C_6F_5CF_3{\bullet}2AlBr_3} & > & \mathbf{CCl_4{\bullet}2AlBr_3} & > & \mathbf{CH_2Br_2{\bullet}\ AlBr_3} \\
\mathbf{75\%,\ 1h} & & \mathbf{50\%,\ 1h} & & \mathbf{36\%,\ 2h} & & \mathbf{29\%,\ 2h} & & \mathbf{22\%,\ 3h}
\end{array}$$

Thus, $CBr_4{\bullet}2AlBr_3$ is the most active among the studied catalysts.

In all cases, the above bromination is accompanied by reduction of initial polyhalomethanes. In other respects, however, ethane bromination differs from that of higher alkanes and cycloalkanes. First, the higher paraffin bromination is a catalytic reaction, while ethane bromination is a stoichiometric one. Second, ethane forms dibromide, while higher alkanes and cycloaklanes give monobrominated products. Third, cycloalkanes and higher homologs of ethane (but not ethane itself) can be brominated by Br_2 in the presence of $AlBr_3$ in CH_2Br_2, although in the absence of CBr_4 these reactions are noticeably less effective.

Two mechanistic paths of bromination of higher alkanes can be postulated. The first assumes the initial alkane hydride abstraction by a superelectrophile, followed by the Br^- addition from Br_2 to an emerging carbocation (Scheme 2).

Scheme 2

$$\begin{aligned}
\mathbf{RH + CBr_3^+} &\longrightarrow \mathbf{R^+ + CHBr_3} \\
\mathbf{R^+ + Br_2} &\longrightarrow \mathbf{RBr + [Br^+]} \\
\mathbf{RH + [Br^+]} &\longrightarrow \mathbf{RBr + H^+}
\end{aligned}$$

The second path involves the initial attack of a superelectrophile on the Br_2 molecule, resulting in a positive bromine species which then attacks alkane, to give brominated products (Scheme 3).

Scheme 3

$$Br_2 + CBr_3^+ \longrightarrow [Br^+] + CBr_4$$
$$RH + [Br^+] \longrightarrow RBr + H^+$$

Concerning the stage of catalyst regeneration, the latter path is probably more significant for active saturated hydrocarbons, rather than for passive low alkanes requiring stronger electrophiles for their activation.

The formation of monobromides in the case of cycloalkanes and higher alkanes, on the one hand, and the formation of dibromide in the case of ethane, on the other, is probably due to the milder conditions of reactions for the former, in consequence of which, olefins are not produced (i. e., the stage **(b)** of Scheme 1 is not realized).

The nature of active complexes generated in the polyhalomethane• $2AlBr_3$ systems in the presence of Br_2 is not quite clear. According to the quantum-chemical calculation,[12] the bromenium cation complexes $CBr_3^{+\cdots}Y^-$ ($Y=AlBr_4^-$, $Al_2Br_7^-$) with the monocoordinated positively charged bromine atom — rather than the more highly charged, but considerably more thermodynamically unstable bromenium dication complexes $Y^-Br^+=C=Br^+Y^-$— seem to be the real intermediates in reactions with $CZX_3 \bullet 2AlBr_3$ (Z=H, Br; X=Cl, Br). On the contrary, in reactions with $C_6F_5CF_3 \bullet 2AlBr_3$ the active species is probably the complex of the reported $C_6F_5CF_2^+$ cation.[13]

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8. At $[Br_2] \geq [CBr_4 \bullet 2AlBr_3]$ the homogenous solution is formed.
9. The yields of brominated products are calculated according to the following formal equations: $C_2H_6 + 1/2Br_2 \rightarrow C_2H_5Br$; $C_2H_6 + Br_2 \rightarrow C_2H_4Br_2$.
10. Bromination of some alkanes and cycloalkanes by $CHBr_3 \bullet 2AlBr_3$ was reported in [5].
11. In this and all the following cases, the yields of bromides are calculated according to the equations: $RH + Br_2 \rightarrow RBr + HBr$; $RH + 2Br_2 \rightarrow R'Br_2 + 2HBr$.
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