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# Reactivity of alkali and alkaline earth metal tetrafluorobromates towards aromatic compounds and pyridine

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ABSTRACT

The bromination activity of tetrafluorobromates of alkali and alkali-earth metals increases in the order $KBrF_4$, $CsBrF_4$, $RbBrF_4$ and $Ba(BrF_4)_2$. The most active tetrafluorobromate—$Ba(BrF_4)_2$ is able to selectively brominate the deactivated aromatic compounds nitrobenzene and 4-nitrotoluene, but not the activated compounds benzene and toluene. In all cases bromination of methyl groups of methylbenzenes does not occur. $Ba(BrF_4)_2$ forms the known complex $C_6H_5N{\cdot}BrF_3$ when reacted with pyridine. Due to dilution by inert $BaF_2$, this pyridine-based complex is air stable and can be considered as safer and more convenient reagent in comparison with the original fluorobromates; it can selectively brominate benzene and toluene in contrast with tetrafluorobromates.

## 1. Introduction

Bromine trifluoride and other bromine fluorides are compounds with high fluorinating or brominating ability [1,2]. Particularly Rozen and Lerman showed that $BrF_3$ can selectively brominate highly deactivated arenes in the presence of bromine; at the same time pure $BrF_3$ gives complex mixture of products in the cases of benzene and activated arenes [3]. Also $BrF_3$ is a highly toxic and dangerous compound, with extremely high reactivity [2], especially with organic compounds which lead to explosions. These properties have restrained widespread application of $BrF_3$ in synthetic chemistry and its usage requires special techniques.

Tetrafluorobromates of alkali and alkali-earth metals (TFB), with the common formula $M_x(BrF_4)_y$, can be considered as $BrF_3$-based complexes which are safer and more convenient for use than $BrF_3$ [4–9]. However, there is no systematic data about the reactivity of TFB towards organic compounds. Recently it was shown that the air-stable complex $BrF_3$-KHF could be used in the desulfurizing fluorination of benzylic sulfides and dithioacetals at room temperature in $CH_2Cl_2$ solution [6]. Nevertheless, the chemical properties of such compounds in organic reactions are not well-researched and the influence of the $M^{n+}$ cation is not explored.

Herein we describe chemical properties of known fluorobromates: $KBrF_4$, $CsBrF_4$, $RbBrF_4$ [7,8] and the recently described $Ba(BrF_4)_2$ [9] in reactions with aromatic compounds and pyridine.

## 2. Results and discussion

### 2.1. Reactions between $KBrF_4$, $CsBrF_4$, $RbBrF_4$ and $Ba(BrF_4)_2$ with nitrobenzene and 4-nitrotoluene

Initially the examined TFBs caused strong explosions and decomposition of the initially pure and dry organic substrates to unidentifiable mixtures. However, mild and selective conditions were found in the cases of nitrobenzene **1** and 4-nitrotoluene **2** to give the corresponding *m*-bromonitroarenes **1a** and **2a** with good yields. Addition of TFBs to substrates **1**, **2** in dry $ClF_2CCCl_2F$ (Freon R113) was performed at −25 °C with strong stirring before the cooling bath was removed. The reaction mass was stirred at 45 °C for 5 h; the gradual gas evolution was observed. The absence of $F_2$ in the gaseous products was determined by a qualitative test with potassium iodide [10]. Analysis of the reaction mixture was performed using GC–MS and it was found that there were no fluorine-containing organic products.

Preparative yields of **1a** and **2a** (Table 1) in cases of different fluorobromates showed the reactivity order $KBrF_4 < RbBrF_4 < CsBrF_4 << Ba(BrF_4)_2$. It was also found that strongly deactivated 1,3-dinitrobenzene is inert to $Ba(BrF_4)_2$.

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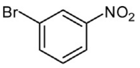
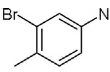
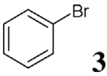
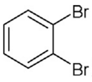
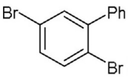
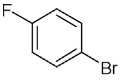
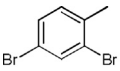
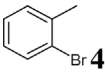
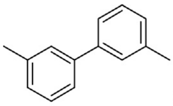
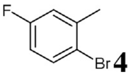
**Table 1**
Reactions of $KBrF_4$, $CsBrF_4$, $RbBrF_4$ and $Ba(BrF_4)_2$ with arenes **1**–**4**.[a]

| Substrate | Reagent | Product | Yield (%) |
|---|---|---|---|
| Nitrobenzene **1** | $KBrF_4$<br>$RbBrF_4$<br>$CsBrF_4$<br>$Ba(BrF_4)_2$ |  **1a** | 12[b]<br>14[b]<br>24[b]<br>84[b] |
| 4-Nitrotoluene **2** | $Ba(BrF_4)_2$ |  **2a** | 87[b] |
| Benzene **3** | $Ba(BrF_4)_2$ |  **3a** | 16[c] |
| | |  **3b** | 34[c] |
| | |  **3c** | 17[c] |
| | | Ph-Ph **3d** | 12[c] |
| | |  **3e** | 8[c] |
| Toluene **4** | $Ba(BrF_4)_2$ |  **4a** | 24[c] |
| | |  **4b** | 14[c] |
| | |  **4c** | 17[c] |
| | |  **4d** | 9[c] |

[a] Representative procedure: arenes (4 mmol), TFB (2 mmol), Freon R 113 (4.1 mL).

[b] Isolated yields.

[c] GC.

### 2.2. Reactions of $Ba(BrF_4)_2$ with benzene and toluene

At the same time benzene **3** and toluene **4** reacted unselectively with $Ba(BrF_4)_2$ under the described conditions to give inseparable mixture. In these cases in according to GC data, the main products were bromoarenes **3a**, **b** and **4a**, **b** with various biphenyls **3c**, **d** and **4c** and traces of bromo-fluoro arenes **3e** and **4d** were also identified. The formation of biphenyls **3c**, **3d** and **4c** shows that Ba$(BrF_4)_2$ also possesses oxidation ability towards non-deactivated arenes. It is important to note that no products of methyl group benzylic bromination with methylarenes **2**, **4** was observed which shows that the mechanism is electrophilic rather than free-radical.

### 2.3. Reaction of $Ba(BrF_4)_2$ with pyridine

It is well-known that pyridine **5** has low reactivity in electrophilic bromination processes [11]. In the reaction of pyridine **5** with $Ba(BrF_4)_2$ we observed the exothermic (temperature increase to 40 °C) decomposition of $Ba(BrF_4)_2$ to $BaF_2$. No pyridine or pyridine-based compounds were observed in the liquid phase, but the solid phase contained a pyridine derivative with high reactivity. This solid phase product rapidly exploded upon the addition of water with the formation of bromine, hydrogen fluoride and pyridine. It is known that the $C_6H_5N{\cdot}BrF_3$ complex **6** can be obtained from the reaction of pyridine and $BrF_3$ [12,13]. Therefore it is proposed that the $C_6H_5N{\cdot}BrF_3$ complex diluted by $BaF_2$ was formed in the explored reaction (Fig. 1).

The pure $C_6H_5N{\cdot}BrF_3$ complex was unstable and rapidly decomposed in air and upon contact with water, however its lifetime in $CHCl_3$, $CFCl_3$ suspensions was about 8–10 h. The high reactivity of **6** did not allow acquisition of liquid or solid state NMR spectra of this compound [13,14].

Dilution of complex **6** by $BaF_2$ (Fig. 1) lowers its reactivity and makes it easier to handle. The diluted complex can be stored in dry air indefinitely. In contrast to $Ba(BrF_4)_2$ it does not react explosively with organic compounds. At the same time complex **6**-$BaF_2$ has sufficient reactivity and unlikely to $BrF_3$ and $Ba(BrF_4)_2$ can selectively brominate not only the deactivated arenes nitrobenzene **1** and 4-nitrotoluene **2**, but even the activated arenes benzene **3** and toluene **4** (Table 2).

These experiments showed that **6**-$BaF_2$ is a milder brominating reagent than $BrF_3$ and even $Ba(BrF_4)_2$. It is important to note no benzylic bromination and fluorine-containing products were formed. It is also interesting that the reaction of **6**-$BaF_2$ and toluene **4** has unusually high *ortho*-selectivity, which leads to the formation of *o*-bromotoluene **4b** as a single isomer. Such high *ortho*-selectivity is rare in the bromination of toluene. Usually there is high *para*-selectivity [11], while *ortho*-selective bromination can be achieved using N-bromosuccinimide in the presence of $NaHCO_3{\cdot}SiO_2$ with toluene **4** in 20% conversion only [15].

The mechanism of the observed TFB brominating activity is unclear and requires further research. The reaction between arenes and insoluble TFB causes its decomposition; this means that reaction starts from the formation of some complexes probably $M\delta^-$–$\delta^+BrF_3$–Ar on the surface of TFB. We can also propose that their decomposition leads to the formation of hypervalent bromine aromatic intermediates, aryl-difluoro-$\lambda^3$-bromanes ($ArBrF_2$) [16], which after the reaction mass quench by $H_2O$, $NaNO_2$ and $CaCl_2$ (see experimental procedure) give the corresponding aryl bromides. The proposed hypothesis at least provides an explanation of the observed electrophilic type of bromination.

It is also possible to consider an alternative reaction based on the formation of $Br_2$ and $F_2$ (with following *in situ* formation of bromine fluorides) upon the decomposition of TFB by arenes. However, this idea contradicts the absence of $F_2$ in the gaseous

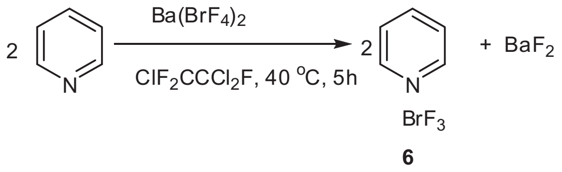


**Fig. 1.** Formation scheme of $C_6H_5N{\cdot}BrF_3$ complex **6** diluted by $BaF_2$.

**Table 2**
Reactions of $Py\cdot BrF_3(BaF_2)$ with arenes **1**–**4**.[a]

| Substrate | Product | Yield% |
|---|---|---|
| **1** | **1a** | 23[b] |
| **2** | **2a** | 19[b] |
| **3** | **3a** | 89[b] |
| **4** | **4b** | 87[c] |

[a] Representative procedure: arenes (4 mL), 6-$BaF_2$ (1.92 mmol), rt.
[b] Isolated yields.
[c] GC–MS.

reaction products and fluoroorganic products (except from minor products **3e** and **4d**).

In summary we have shown for the first time that $Ba(BrF_4)_2$ and its complex with pyridine diluted by $BaF_2$ are convenient reagents and they can be considered as safe forms of $BrF_3$. These compounds have strong and selective electrophilic bromination abilities towards not only deactivated nitrobenzenes but also benzene and toluene.

## 3. Experimental section

All chemicals were analytical grade and used as purchased without further purification. TFBs were synthesized using previously described methods [7–9] directly before use. Pyridine was of analytical grade and was additionally dried using metal sodium. Freon R 113 was of analytical grade and was additionally dried using metal sodium. All experiments with pyridine and its' derive compounds were performed in dry box installation with less than 5 ppm $H_2O$ concentration. $^1$H, $^{13}$C NMR spectra were recorded on a Bruker AC 300 spectrometer with tetramethylsilane (TMS) as the internal standard, solvents $CDCl_3$. Multiplicities of signals are described as follows: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet. Melting points were determined on melting point system MP50. The identification of obtained compounds was performed by comparing the analytical and physical-chemical characteristics as the authentic sample synthesized by known methods. GC–MS analysis was performed on Agilent 7890A (Agilent Technologies, USA) combined with a mass detector Agilent 5975C, a carrier gas – helium. Products identification was performed by mass spectra and retention times (RT) in comparison with authentic samples. Reaction progress was monitored by TLC with UV detection using Silufol UV-254.

### *3.1. Reactions of TFBs with arenes **1**–**4***

TFBs were synthesized using previously described methods [7–9] directly before use. Corresponding arene (4 mmol) was dissolved in Freon R 113 (4.1 mL), and cooled to −25 °C. The corresponding TFB (2 mmol) was slowly added to the arene solution with vigorous stirring and the cooling bath was removed. The reaction mass was stirred at 45 °C for 5 h. After reaction completion the reaction mass was treated by $H_2O$ and filtered to remove the metal fluoride precipitate. The liquid phase was treated by 10% aqueous $NaNO_2$ in order to remove traces of bromine and with 30% aqueous $CaCl_2$ to remove the $F^-$ anion. Freon R 113 was evaporated from the organic phase and the obtained product purified by silica gel flash chromatography, eluent hexane:EtOAc.

*3-Bromonitrobenzene* (***1a***). Following general protocol using **1** and $Ba(BrF_4)_2$ the **1a** was obtained as yellow crystals (yield 84%), mp 52 °C. RT: 12.81 min. GC–MS, 70 eV, *m*/*z* (rel. int): 30 (26), 50 (55), 75 (86), 143 (21), 155 (100), 201 (92). $^1$H NMR (300 MHz, $CDCl_3$) *δ:* 7.44 (1H, dd, *J* = 8.7, 1.5 Hz), 7.83 (1H, d, *J* = 8,7 Hz), 8.15 (1H, dd, *J* = 8.7, 1.5 Hz), 8.36 (1H, d, *J* = 1.5 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) *δ:* 122.1 (C-3), 122.8 (C-6), 126.7 (C-2), 130.6 (C-5), 137.6 (C-4), 148.7 (C-1).

*2-Bromo-4-*nitrotoluene (***2a***). Following general protocol using **2** and $Ba(BrF_4)_2$ the **2a** was obtained as yellow crystals (yield 87%), mp 76 °C. RT: 15.04 min. GC–MS, 70 eV, *m*/*z* (rel. int): 30 (46), 39 (28), 63 (63), 78 (26), 90 (100), 169 (27), 185 (18), 199 (1), 215 (58). $^1$H NMR (300 MHz, $CDCl_3$) *δ:* 2.5 (3H, s), 7.4 (1H, d, *J* = 8.4 Hz), 8.05 (1H, dd, *J* = 8.4, 2.0 Hz), 8.37 (1H, d, *J* = 2.0 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) *δ:* 23.2 ($CH_3$), 122.2 (C-5), 124.9 (C-2), 127.4 (C-3), 131.1 (C-6), 145.8 (C-1), 146.8 (C-4).

*Bromobenzene* (***3a***). Yield 16%, GC data. RT: 5,18 min. GC–MS, 70 eV, *m*/*z* (rel. int): 12 (1), 26 (4), 38 (16), 51 (49), 77 (100), 156 (75).

*1,2-Dibromobenzene* (***3b***). Yield 34%, GC data. RT: 10.71 min GC–MS, 70 eV, *m*/*z* (rel. int): 26 (1), 50 (19), 75(28), 118 (12), 155 (38), 236 (100).

*2,5-dibromo-1,1′-biphenyl* (***3c***). Yield 17%, GC data. RT: 16.63 min. GC–MS, 70 eV, *m*/*z* (rel. int): 50 (19), 76 (37), 98 (8), 126 (11), 152 (100), 312 (87).

*Biphenyl* (***3d***). Yield 12%, GC data. RT: 13.72 min. GC–MS, 70 eV, *m*/*z* (rel. int): 27 (1), 39 (5), 51 (16), 63 (11), 76 (22), 89 (4), 102 (7), 115 (7), 128 (8), 139 (4), 154 (100).

*1-Bromo-4-fluorobenzene* (***3e***). Yield 8%, GC data. RT: 4.95 min. GC–MS, 70 eV, *m*/*z* (rel. int): 25 (2), 37 (4), 50 (12), 62 (5), 75 (36), 95 (100), 174 (96).

*2,4-Dibromo-1-methylbenzene* (***4a***). Yield 24%, GC data. RT: 12.65 min. GC–MS, 70 eV, *m*/*z* (rel. int): 44 (11), 63 (20), 90 (41), 169 (59), 250 (100).

*1-Bromo-2-methylbenzene* (***4b***). Yield 14%, GC data. RT: 7.77 min. GC–MS, 70 eV, *m*/*z* (rel. int): 27 (2), 39 (17), 51 (11), 65 (21), 77 (1), 91 (100), 170 (40).

*3,3′-Dimethyl-1,1′-biphenyl* (***4c***). Yield 17%, GC data. RT: 16.63 min. GC–MS, 70 eV, *m*/*z* (rel. int): 25 (2), 39 (5), 51 (6), 63 (8), 76 (8), 89 (6), 115 (8), 128(7), 152 (10), 167 (37), 182 (100).

*1-Bromo-4-fluoro-2-methylbenzene* (***4d***). Yield 9%, GC data. RT: 7.53 min. GC–MS, 70 eV, *m*/*z* (rel. int): 15 (2), 39 (14), 57 (26), 83 (41), 109 (100), 190 (51).

### *3.2. Reactions of TFBs with pyridine **5***

Pyridine (4 mmol) was dissolved in Freon R113 (4.1 mL) and cooled to −25 °C. $Ba(BrF_4)_2$ (2 mmol) was added to the pyridine solution with vigorous stirring and stirred for 5 h to prevent solid product agglomeration. The obtained white solid product **6** in a mixture with $BaF_2$ was decanted from Freon 113 and used for further experiments without additional purification.

### *3.3. Reactions of **6**-$BaF_2$ with arenes **1**–**4***

**6**-$BaF_2$ (1.92 mmol) was added to corresponding arene **1**–**4** (5 mL) at room temperature and stirred for 5 h. The reaction mixture was filtered from solid $BaF_2$, liquid products were analysed by GC–MS and bromoarenes **1a**, **2a** and **3a** were isolated by silica gel flash chromatography, eluent hexane:EtOAc – 3:1 (v/v).

*3-Bromonitrobenzene* (***1a***). Following general protocol using **1** and **6**-$BaF_2$ the **1a** was obtained as yellow crystals (yield 23%). RT: 12.81 min. GC–MS, 70 eV, *m*/*z* (rel. int): 30 (26), 50 (55), 75 (86), 143 (21), 155 (100), 201 (92). $^1$H NMR (300 MHz, $CDCl_3$) *δ:* 7.44 (1H, dd, *J* = 8.7, 1.5 Hz), 7.83 (1H, d, *J* = 8,7 Hz), 8.15 (1H, dd, *J* = 8.7, 1.5 Hz), 8.36 (1H, d, *J* = 1.5 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) *δ:* 122.1 (C-3), 122.8 (C-6), 126.7 (C-2), 130.6 (C-5), 137.6 (C-4), 148.7 (C-1).

*2-Bromo-4-nitrotoluene* (***2a***). Following general protocol using **2** and **6**-$BaF_2$ the **2a** was obtained as yellow crystals (yield 19%). RT: 15.04 min. GC–MS, 70 eV, *m*/*z* (rel. int): 30 (46), 39 (28), 63 (63), 78 (26), 90 (100), 169 (27), 185 (18), 199 (1), 215 (58). $^1$H NMR (300 MHz, $CDCl_3$) *δ:* 2.5 (3H, s), 7.4 (1H, d, *J* = 8.4 Hz), 8.05 (1H, dd, *J* = 8.4, 2.0 Hz), 8.37 (1H, d, *J* = 2.0 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) *δ:* 23.2 ($CH_3$), 122.2 (C-5), 124.9 (C-2), 127.4 (C-3), 131.1 (C-6), 145.8 (C-1), 146.8 (C-4).

*Bromobenzene* (***3a***). Following general protocol using **3** and **6**-$BaF_2$ the **3a** was obtained as yellow oil (yield 89%). RT: 5.18 min. GC–MS, 70 eV, *m*/*z* (rel. int) 12 (1), 26 (4), 38 (16), 51 (49), 77 (1 00), 156 (75). $^1$H NMR (300 MHz, $CDCl_3$) *δ*: 7.2 (2H, m), 7.47 (3H, m). $^{13}$C NMR (75 MHz, $CDCl_3$) *δ:* 122.2 (C-1), 126.7 (C-4), 129.9 (C-3,5), 131.3 (C-2,6).

*1-Bromo-2-methylbenzene* (***4b***). Yield 87%, GC data. RT: 7.77 min. GC–MS, 70 eV, *m*/*z* (rel. int): 27 (2), 39 (17), 51 (11), 65 (21), 77 (1), 91 (100), 170 (40).

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## References

[1] S. Rozen, Adv. Synth. Catal. 352 (2010) 2691–2707.
[2] S. Rozen, Acc. Chem. Res. 38 (2005) 803–812.
[3] S. Rozen, O. Lerman, J. Org. Chem. 58 (1993) 239–240.
[4] S. Siegel, Acta Crystallogr. 9 (1956) 493–495.
[5] K.O. Christe, C.J. Schack, Inorg. Chem. 9 (1970) 1852–1858.
[6] T. Shishimi, S. Hara, J. Fluorine Chem. 168 (2014) 55–60.
[7] S. Ivlev, P. Woidy, V. Sobolev, I. Gerin, R. Ostvald, F. Kraus, Z. Anorg. Allgem. Chem. 639 (2013) 2846–2850.
[8] S.I. Ivlev, A.J. Karttunen, R. Ostvald, F. Kraus, Z. Anorg. Allgem. Chem. 641 (2015) 2593–2598.
[9] S. Ivlev, V. Sobolev, M. Hoelzel, A.J. Karttunen, T. Müller, I. Gerin, R. Ostvald, F. Kraus, Eur. J. Inorg. Chem (2014) 6261–6267.
[10] J.H. Simons, Fluorine Chemistry, vol. II, Academic Press Inc, New York, 1954.
[11] L.G. Voskressensky, N.E. Golantsov, A.M. Maharramov, Synthesis 48 (2016) 615–642.
[12] D. Naumann, E. Lehmann, J. Fluorine Chem. 5 (1975) 307–321.
[13] Y. Hagooly, S. Rozen, Org. Lett. 14 (2012) 1114–1117.
[14] T. Delgado-Abad, J. Martinez-Ferrer, J. Reig-Lopez, R. Mello, R. Acerete, G. Asensio, M. Gonzalez-Nunez, RSC Adv. 4 (2014) 51016–51021.
[15] A. Rahman, S.B. Jonnalagadda, Synth. Commun. 42 (2012) 1091–1100.
[16] U. Farooq, A.A.-H. Shah, T. Wirth, Angew. Chem. Int. Ed. 47 (2008) 1018–1020.