# Evidence of Halogen Exchange between Gaseous Halogenated Alkanes and Solid Alkali Halides obtained by Field Desorption Mass Spectrometry

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Summary Field desorption mass spectrometry is used as a probe for heterogeneous halogen exchange reactions between alkali halides and different mono- and dihalogenated alkanes.

Little is known about halogen exchange reactions on salt surfaces exposed to gaseous halogen-containing compounds. Only the isotope exchange between $Me^{131}I$ and $Na^{127}I$ has been investigated in detail.[1] This communication reports the use of field desorption (FD) mass spectrometry for the study of heterogeneous halogen exchange between solid alkali halides and gaseous halogenated alkanes. In the FD of alkali halides, $(\text{alkali}_{n+1}\text{halogen}_n)^+$ ions with $n \geqslant 0$ are formed, the ion species depending on the composition of the salt surface.[2] This allows products of heterogeneous halogen exchange reactions to be identified.

For studying the heterogeneous halogen exchange a conventional FD mass spectrometer was used. The alkali halides were deposited on untreated 10 $\mu$m tungsten wire emitters from aqueous solution. The salt layer was several $\mu$m thick. After evaporation of the solvent the halogenated alkanes were introduced into the ion source of the FD mass spectrometer at a pressure of 130 Pa. The wire was then heated to 500—550 K for 15 min. During the reaction time no ion source potential was applied to avoid any effect of an external field on the exchange reaction. The salt layer was analysed by FD after evacuation of the ion source. The ion signal of the exchange product was taken as a measure of the extent of the exchange reaction.

TABLE. Heterogeneous halogen exchange between halogenated alkanes and lithium iodide.[a]

| Gas | Exchange product (FD-ion) |
|---|---|
| EtBr | $Li_2Br^{+b}$ |
| $Pr^nCl$ | $Li_2Cl^+$ |
| $Pr^iCl$ | $Li_2Cl^+$ |
| $Pr^nBr$ | $Li_2Br^+$ |
| $Pr^iBr$ | $Li_2Br^+$ |
| $Bu^sBr$ | $Li_2Br^+$ |
| $Bu^tBr$ | $Li_2Br^+$ |
| $CH_2BrCH=CHCH_2Br$ | $Li_2Br^+$ |

[a] Exchange was not detected with $BrCH_2CH_2Br$, $MeCHBr$-$CH_2Br$, $CH_2BrCH_2CH_2Br$, or $CH_2BrCH_2CH_2CH_2Br$. [b] Weak signal.

Results for the halogen exchange between LiI and several halogenated alkanes are in the Table. Intensity differences indicate that the extent of halogen exchange increases from chlorine to bromine and from primary to tertiary halogenated alkanes. With the dihalogenated alkanes exchange products were detected with 1,4-di-bromobut-2-ene but not with the other compounds in footnote a to the Table. This is most probably due to a variation in the halogen binding energy which is lower for 1,4-dibromobut-2-ene, suggesting that the activation energy of the halogen exchange reaction is strongly dependent on the halogen binding energy. In addition it was found that the rate of halogen exchange is much higher with LiI, NaI, and LiCl than with NaCl and KCl.

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