# Thermal and catalytic hydrodehalogenation of halon 1301 with methane

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## Summary

There **are** severe restrictions on the use of halons in Australia since the government has banned them for all but essential use, and legislated their withdrawal. The long term storage of these chemicals is costly and is delaying the inevitable need for proper and complete disposal necessitates the development of new and innovative technologies for the treatment of these materials. We have investigated the gas-phase and surface-catalysed conversion of halon 1301 into reusable products through their reaction with methane. A tubular flow reactor facility was used for all studies which included gas control manifold, three-zone high temperature furnace, gas chromatograph and FTIR for product identification and quantification. **Gas** phase reaction of $CH_4$ with $CF_3Br$ in a $N_2$ bath (molar feed ratio of 1:1:10) at 600°C and residence time ($\tau$) of 2 seconds produced a range of reaction products with $C_2F_6$ and $C_2H_6$ **as** major product species. Minor species including $C_2H_4$, $CF_3CH_3$, $C_2H_2$ and a small number of as-yet unidentified products were also detected. Under all conditions studied, an average of 0.6 moles of $CH_4$ reacted per mole of $CF_3Br$, for both gas-phase and catalytic reactions. A small number of ionexchanged ZSM5 zeolites have been studied as potential catalysts for the title reaction. Enhanced conversion activity was observed for all metal-zeolites examined, although there appears to be little difference in activity between each catalyst. Only relatively minor changes in product selectivity **(as** compared to gas-phase product selectivities) were observed.

## Australian perspective

Unlike other countries such **as** the United States, the Australian government has banned both the production and the use of halons after January 1st, 1996. No recycling of halons after the January deadline is allowed in Australia, whereas in the United States recycling will continue at least for the foreseeable future. Recycling will result in the gradual diminution of halon stocks, the end result being the discharging of these compounds into the atmosphere where they will contribute to the depletion of the ozone in the upper atmosphere. As well as their ozone depleting characteristics, halons also have a high global warming potential (GWP of these compounds as high as 5000 compared to unity for $CO_2$) and thus will also contribute to the greenhouse effect. In Australia, halon stocks are being collected and transported to Melbourne (Victoria), where a recently commisioned plasma-arc destruction facility will convert the halons to environmentally benign byproducts such **as** $H_2O$, $CO_2$ and mineral acids HF, HCl and HBr.

## Destructive disposal techniques

A review of destruction technologies for halon wastes has appeared recently where a number of existing and emerging technologies, such as hydrolysis, steam reforming, dehalogenation, dehydrohalogenation as well **as** a variety of oxidation processes, were evaluated’. These authors recommended further testing and development of many techniques was warranted, of particular concern were the low destruction efficiencies and the possible production of undesirable side-products. Of existing “complete” treatment technologies for halons (including chemical, physical and biological processes), incineration is the most widely adopted technology [2]. In the case of halons, complete combustion would result in the production of $CO_2$, and HX, where X is an *alkyl* halide. Halogen gases ($X_2$) are toxic and difficult to separate and thus their production is not desirable.

There are many problems associated with the use of incinerators. The high cost of safe transportation of the material to the incinerator, the use of ancillary fuels (which can contribute up to 40% of the overall running cost of the process)[3] and the large volume of the reactor needed to ensure adequate residence time in the reactor all contribute to a high overall running cost, It is, however, the emission of both feed and incomplete combustion byproducts from the incinerator which are the cause of most concern, and have inhibited the widespread acceptance of incinerators. Carcinogenic products such as dioxins[4] and phosgene' are just some of the by-products detected in the effluent of incineration processes. The origin of such undesirable species is not clear, though it has been suggested dioxins may form in post-combustion cooling regions of the incinerator[6].

### Hydrodehalogenation

One attractions of hydrodehalogenation is that the reaction takes place in the absence of oxygen. The process involves reacting the halon with hydrogen (either with or without catalyst) to produce mineral acids ($HBr$, $HCl$ or $HF$) and a secondary products, usually hydrocarbons (especially methane) and possibly new HFC compounds. Since banned halons often exist in relatively pure form (as opposed to flue gases containing ppm levels of chlorinated hydrocarbons), it is (potentially) economically feasible to develop a hydrodehalogenation processes to deal with a very specific halocarbon substrate'. For example when halon-1211 reacts with $H_2$, the products could include $CH_2F_2$, (where both Cl and Br halogen atoms have been removed from the parent halon, but both F species remain intact) $HCl$ and $HBr$. Other halocarbons or hydrocarbons may also be produced (such as $C_2F_4$), depending on reaction conditions and type of catalyst.

While a wide range of catalysts have been screened for activity, Group VIII metals (especially Pd) and bimetallic catalysts (usually a noble metal with a transition metal) are most often reported as catalysts for hydrodehalogenation reactions. The substrate most studied has been aromatic halides, and both homogeneous (eg. nickel(II) complexes') and heterogeneous (Pd/C[9]) catalysts have been used. Tetrachloromethane was converted to chloroform over a platinum/MgO catalyst with a $H_2{:}CCl_4$ mole ratio of 5:1[10]. The long lifetime of the catalyst was attributed to the retarding of coke formation by the MgO, and the authors also concluded, using X-ray photoelectron spectroscopy (XPS) analysis of the catalyst, that the active species involved in the reaction was $Pt^{II}$. Palladium-based catalysts have demonstrated great potential for hydrodechlorination of perhalogenated aliphatic CFCs'[1].

The conversion of difluorodichloromethane under hydrogen has been studied over a series of Pd and Pd bimetallics[12]. The product distribution from palladium catalysed reactions of CFCs with hydrogen can be controlled, at least to some extent, if Pd is used in conjunction with Fe or Co. For example, at low substrate partial pressures, methane and $CH_2F_2$ constituted the main reaction products while higher substrate pressures resulted in increased selectivity to $C_2F_4$. It is not clear what mechanism leads to the observed shift in selectivity when the catalyst is changed from a single metal to a bimetallic type catalyst. It has been suggested that both hydrogen and halocarbon molecules are physisorbed on the surface of a single-metal palladium catalyst (a classical Langmuir-Hinshelwood mechanism). However, some experimental data indicate that PdFe and PdCo sites are operative and these bimetallic sites inhibit the co-adsorption of halocarbon and hydrogen. At this hydrogen-depleted adsorption site, coupling of activated halocarbon intermediates may occur leading to short chain formation, such as $CF_2{=}CF_2$. It is possible that within these large domains of PdFe and PdCo sites, halocarbons undergo preferential scission of bromine and chlorine atoms, since C-Br, and C-Cl constitute weaker bonds than C-F. Why $H_2$ adsorption is inhibited on these sites is not clear. Hydrogenolysis of CFC 12 ($CCl_2F_2$) has been studied, an activated carbon supported noble metal catalyst showing high selectivity to HCFC-22 and resistance to poisoning by coke'[3].

### Halon - HF reactions

Most commercial processes involved with the production of CFC alternatives involve reaction of a chlorinated species with HF[14]. A report outlining a catalytic process to convert $CF_3CH_2Cl$ to $CF_3CH_2F$ has recently appeared[15] where the chlorine atom present in the parent halon is replaced with fluorine (see below).

$$CF_3CH_2Cl + HF \dashrightarrow CF_3CH_2F + HCl$$

The catalyst used by the authors was a chromium (III) oxide and the authors showed that activity of the catalyst was proportional to the number of reversibly oxidised sites present on the catalyst. This process forms the **basis** of a number of European and World patents''.

## Halon - methane reactions

Interest in the use of methane as a hydrogen or homologation source has remained strong for a number of **years,** the chief attraction being the relative low cost of **natural** gas (the **main** constituent of which is methane) and its relatively high purity. The challenge in activating methane in the presence of a co-fed substrate is that the catalyst usually will react much faster with the substrate than with methane, effectively blocking the active sites on the surface of the catalyst for activation of methane. Some success in reacting methane has been achieved, as outlined below, and these catalyst systems were used as a guide this investigation. Homogeneous (gas phase) reactions between methane and chlorinated hydrocarbons have been reported[17]. These studies were undertaken at relatively high temperatures, although reaction between methylene chloride and methane were observed. To our knowledge, there are no published reports of catalytic reactions of methane with halons.

## Catalytic activation of methane

Catalytic reaction between methane and a co-fed substrate under reducing reaction conditions has been reported. Alkylation of naphthalene with methane was achieved, catalysed by metal exchanged zeolites and MeAlPO molecular sieves in a batch reactor[18]. Elevated pressure (6.3 MPa) and reaction temperatures were employed and these authors proved methane incorporation into naphthalene using $^{13}CH_4$ isotope studies. Nickel-based catalysts have also been used in the homologation of unsaturated compounds including propene[19], and verification of the incorporation of methane into the butane products was undertaken. The coupling of cyclopentene with methane over supported nickel catalysts produced benzene and toluene as products, $^{13}C$ labelling studies showed incorporation of the methane was taking place, but only to a modest extent. **A** novel approach to methane activation involves a reaction sequence divided into three distinct steps: (1) reaction of methane on a reduced transition metal catalyst, (2) after cooling, adsorption of the olefin with the methane moiety and (3) passing of hydrogen over the catalyst where the higher homologue is desorbed and the cycle is continued. $^{13}C$ labelling studies confirmed methane incorporation into the products, although some self homologation was also taking **place''.**

Superacid catalysts have been used for the reaction of methane with ethylene'' (reaction pressures **up** to 20 MPa) as well **as** for the electrophilic chlorination of methane to methyl chloride[22]. In both these cases, sulfated zirconia was used **as** catalyst, although relatively mild conditions were employed for the reaction of methane with chlorine (240°C, ambient pressure) **as** compared with the ethylene/methane reaction.

Incorporation of methane into halon 1301 could be a possible route to the production of valuable products and this possibility gave impetus to the present investigation. Consider, for example, the reaction of halon 1301 with methane where co-activation of both species **results** in a coupling of these species, a range of products are. feasible including $C_2H_6$, $CF_3H$ and $CF_3CF_3$. If conditions were optimised such that $CF_3CF_3$ production was favoured, it may then be possible to react this species further, probably with HF, to produce $CHF_2$-$CF_3$.

The overall process would then be:

Coupling of methane with halon:

$$CF_3Br + CH_4 \text{ ----> } CH_3CF_3 + HBr$$

Subsequent reaction with HF

$$CF_3CH_3 + 2HF \text{ ----> } CHF_2\text{-}CF_3 + H_2$$

This suggests that methane may not only act **as** possible H donor (**as** an alternative to hydrogen), but as a carbon source in **the** form of CH3. It may thus be possible to make precursors to compounds such **as** $CHF_2$-$CF_3$ which are used **as** halon replacements in refrigeration system.

## Experimental

**A** schematic of the research plan is presented in figure 1. All gas flows including oxygen (>99.9%), methane (>99.9) nitrogen (>99.99%) and halon 1301 (approximately 81% CF3Br and 18% nitrogen) were controlled and metered with electronic mass flow controllers. The gas mixture was feed into a high temperature alumina (99.8%) tubular reactor heated with a 3-zone electric tube furnace. ***An*** alumina-sheathed thermocouple in the **annular** space in the reactor was used for reference and temperature control. Residence time experiments were performed either by altering flow rates of all feed species or by using alumina tubes of differing internal diameters. After reacting, the (heated) post-reaction gaseous effluent stream was directed through a caustic scrubber and finally either to an MTI gas chromatograph or to a FTIR gas **cell** for product analysis. External **standards** were used where. available to identify and quantify reaction products, especially light hydrocarbon gases. Identification of fluorinated products was achieved through the **use** of the FTIR cell and subsequent comparison with library database spectra. Using these techniques, all major products were determined, although there **are** a number of minor products yet to be identified. Mineral acids trapped in the scrubber were periodically analysed by ion chromatography.

Ion exchanged ZSM5, (Zeolyst International, $SiO_2/Al_2O_3$ ratio of *50)* were prepared by adding catalyst to a nitrate solution of the **metal** ion to be exchanged and evaporating the solution to **dryness. The** metal loading of the zeolite (in all cases 10%) was predetermined by controlling **the** volume and concentration of the nitrate solution.

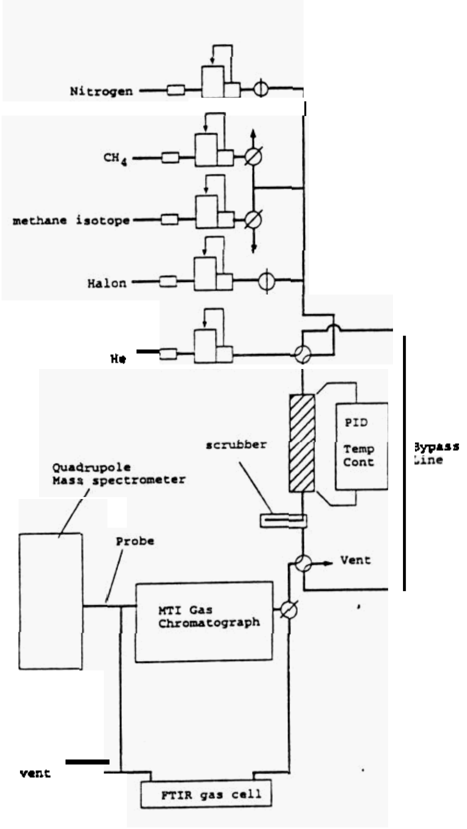

Figure 1. Experimental Facility

### Gas-Phase reaction of $CF_3Br$ with $CH_4$

**The results** of the reaction of $CH_4$ with $CF_3Br$ in a nitrogen bath (molar flow **rate** of 1:1:10 for $CF_3Br:CH_4:CF_3Br$) at various residence times **are** presented in figures **2** and 3. Conversion products were detected at 500°C. and **as** expected higher conversions of both feed species were observed with increasing temperature and longer residence times. In contrast, pyrolysis experiments **of** $CF_3Br$ in a nitrogen bath under flow conditions similar to those for methane reaction no conversion products were observed below a reaction temperature of 725C. Clearly, methane is an important reactant gas to facilitate and maintain reaction of $CF_3Br$. **The** pyrolysis experiments were performed not only to establish a baseline of activity for $CF_3Br$ reactivity but also to examine the propensity of $CF_3$ **radials** produced during pyrolysis to couple to $C_2F_6$. Curiously, only trace quantities ***of*** $C_2F_6$ were observed during $CF_3Br$ pyrolysis experiments, even **at** the highest temperature and conversions examined 800C and X = 0.09. The relative conversion rates for both methane and $CF_3Br$ were constant and almost completely independent of residence **time.** The overall stoichiometry of the reaction observed experimentally was 0.6 moles of $CH_4$ reacted per mole of $CF_3Br$. **The** production of a range of unsaturated hydrocarbon products ($C_2H_4$ and $C_2H_2$) observed is consistent with the lower mole ratio of $CH_4:CF_3Br$ reaction observed.

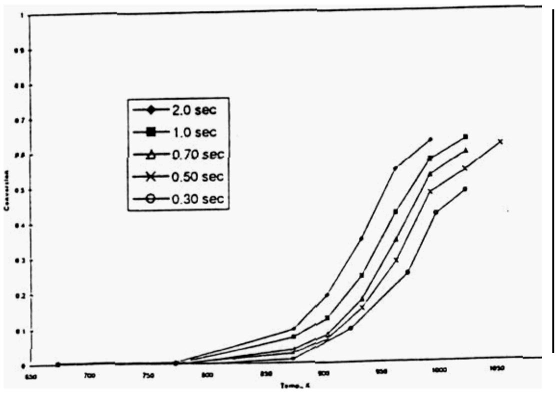

Figure **2**

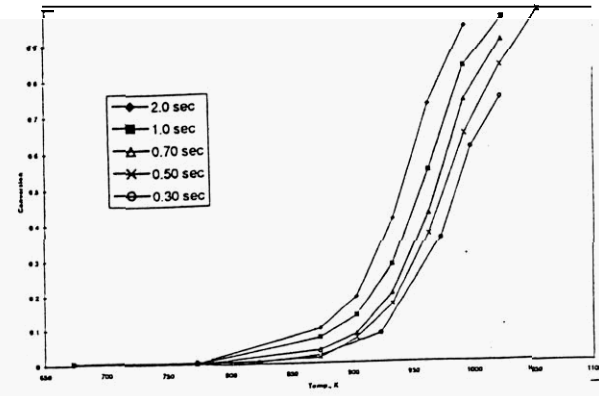

**Figure** 3

Gas-phase conversion **of** $CH_4$ (figure 2) and $CF_3Br$ (figure **3)** vs temperature **at** various residence times ($\tau$ = 0.3, **0.4,** 0.8, 1.6 ). Feed composition 1:1:10 mol ratio of $CH_4:CF_3Br:N_2$.

The initiation step in the overall process would probably be the thermal cleavage of $CF_3Br$

$CF_3Br$ ----> $CF_3$ + Br, thus creating a radical pool.

Hydrogen abstraction from $CH_4$ can then take place between the radicals thus produced and the abundant hydrocarbon gas:

Br + $CH_4$ ----> HBr + $CH_3$

$CF_3$ + $CH_4$ ----> $CF_3H$ + $CH_3$.

**As** conversion of $CF_3Br$ and $CH_4$ increases, so does the relative concentration of $CH_3$ and $CF_3$ radicals, thus increasing the probability of coupling between these species to form $C_2H_6$ and $C_2F_6$. Other (termination) coupling reactions can also take place, such as

CF3 + CH3 ----> $CF_3CH_3$ and

$CH_3$ + Br ----> $CH_3Br$

*All* the stable products discussed above were produced during gas-phase and zeolite-catalysed reaction. The major products detected were $C_2H_6$ and $C_2F_6$, consistent with the above mechanism. Other minor species were also produced and can be explained as follows. The increasing concentration of $C_2H_6$ as conversion increase (due to coupling of $CH_3$ radicals) now competes with $CH_4$ for reaction with $CF_3$ or Br radicals, thus re-entering the reaction pool. Although present in lower concentration than $CH_4$, the lower relative bond strength of the C-H bond in $C_2H_6$ vs $CH_4$ suggests that it will react faster than the methane, thus effectively competing with CH4.

Br + $C_2H_6$ ----> HBr + $C_2H_5$
or
CF3 + $C_2H_6$ ----> $CF_3H$ + $C_2H_5$.

Under these conditions, $C_2H_5$ can quickly decompose to $C_2H_4$, creating a secondary hydrocarbon species which, in turn, can now also re-enter the hydrocarbon pool. **A** similar argument can be extended to the resulting formation of $C_2H_2$ from $C_2H_4$. The end result of these secondary reaction process is to decrease the overall C:H ratio of product hydrocarbons, **thus** leading to the observed lower stoichiometry.

## Zeolite-catalysed reaction **of** $CF_3Br$ with $CH_4$

Zeolite catalysed conversion ***of*** halogenated hydrocarbons have been reported both in the open[23] and patent[24] literature. Zeolite ZSM5 is a synthetic zeolite, and is used for a variety of hydrocarbons processes including the conversion of methanol to gasoline. The **aim** of this small screening trial was to determine whether ion-exchanged ZSM5 catalysts could influence either the activity or selectivity of the title reaction. The results of this screening trial are presented in figures **4** and 5.

*All* of the catalysts **examined** catalysed reaction, but the resultant activity appeared to be almost independent of the ion-exchanged metal form of the zeolite. **A** comparison of the conversion of $CH_4$ and $CF_3Br$ under similar reaction conditions is presented in figures **4** and 5. Figure **4** also includes a comparison of $CF_3Br$ pyrolysis under these conditions. Clearly the MnZSM5 zeolite catalyst enhanced conversion of both feed species for a given set of reaction conditions, as does the other ion-exchanged zeolites (conversion levels of the other zeolites CuZSM5 and CoZSM5 were virtually identical to that of MnZSM5). Similar to gas phase reactions, the $CH_4$:$CF_3Br$ conversion ratio was less than 1, approximately **0.65** over the temperature range examined for all of the zeolites studied. Reaction temperatures were restricted to below 600°C for zeolite studies as above these temperatures HF formation was detected. One of the aims of catalyst development is to minimise fragmentation of the $CF_3$ moiety and thus catalyst trials were performed below temperatures where this species is produced.

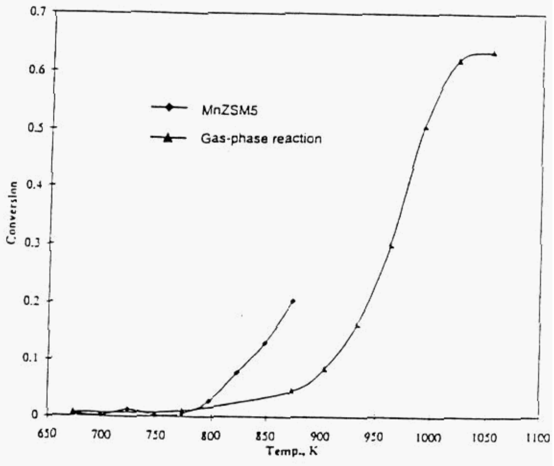

Figure 4

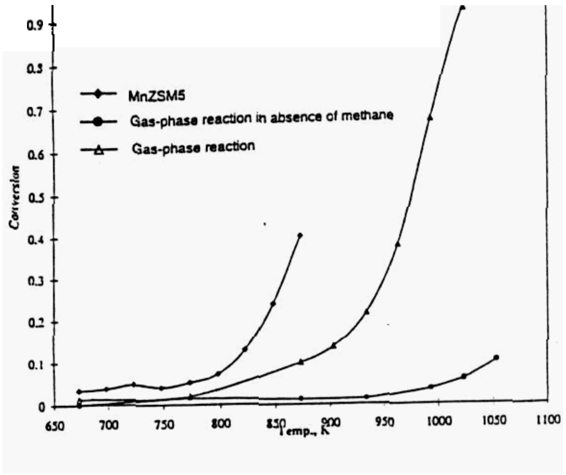

Figure **5**

Comparison of MnZSM5 catalysed conversion of CH, (figure 4) and $CF_3Br$ (figure 5) vs temperature and gas phase conversion levels. All zeolites were pre-treated in a nitrogen stream at 400C before being exposed to feed stream. The inlet feed composition of $CH_4$:$CF_3Br$:$N_2$ was 1:1:10.

## Future work

The authors intend to continue screening various supported zeolites, in particular focussing on Group VIII metal-exchanged ZSM5 catalysts. In addition to catalyst screening, we intend to confirm incorporation of methane-based carbon moieties by preforming experiments with $^{13}C$-labelled $CH_4$. Using an on-line mass spectrometer (currently being commisioned), the authors will determine the extent of coupling between $CF_3Br$ and $CH_4$ species, as well as determining what species is most responsible for coke formation by measuring the mole fraction of $^{13}C$ in the coke.

## Acknowledgments

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