# Gas-phase Alkylation and Halogenomethylation by Free Dialkylhalogenonium and Halogenomethylium Ions [1]

By **Maurizio Speranza** * and **Nicola Pepe**, Laboratorio di Chimica Nucleare del C.N.R., 00016 Monterotondo Stazione, Roma, Italy
**Romano Cipollini**, Istituto Chimico, Università di Camerino, 62032 Camerino, Macerata, Italy

Dimethylhalogenonium ions from the $\gamma$-radiolysis of methyl halides were allowed to react in the gas phase with selected substrates, containing either a $\pi$- or an $n$-type nucleophilic centre. The reactions were studied at $CH_3X$ pressures ranging from 100 to 760 Torr, in the presence of a thermal radical scavenger ($O_2$) and variable concentrations of an added base ($NH_3$). Dimethylfluoronium ions readily react with all the substrates investigated, yielding methylated products, whose isomeric composition appreciably depends on the pressure of the gaseous system. Their attack on toluene leads to an intramolecular distribution (*para*/0.5 *meta* = 2.5) typical of a gas-phase electrophilic displacement process, whereas their substrate selectivity reveals the influence of steric hindrance for the most encumbered substrates. On the other hand, dimethylchloronium and dimethylbromonium ions sharply discriminate between $n$- and $\pi$-type basic centres, showing much greater selectivity than dimethylfluoronium ions. The reactivity and selectivity features of other electrophiles, formed in minor concentrations from the radiolysis of the halides, *i.e.* the halogenomethylium ions, were also examined. The mechanisms of the gas-phase alkylations are discussed, and compared with those of different gaseous electrophiles and with those of Friedel–Crafts alkylating agents. It is concluded that the behaviour of condensed-phase methylating species and gas-phase dimethylfluoronium ions display significant analogies, traced to their common mode of attack on aromatic substrates.

AROMATIC alkylation by alkyl halides, under Friedel–Crafts conditions, is of wide application in organic chemistry and chemical technology.[2] Mechanistic studies showed that, in these systems, several different alkylating agents may be active, whose weight is strictly related to the structure of their precursor(s), the nature of both the halogen atom and the Lewis-acid catalyst involved, and the properties of the solvent.[3] The intervention of individual alkylating species has been proved, under favourable circumstances, such as alkyl halide Lewis-acid complexes, stable carbenium ions, or dialkylhalogenonium ion salts.[4] The degree to which dialkylhalogenonium ions are involved in Friedel–Crafts reactions has been the subject of a number of spectroscopic and kinetic investigations.[4,5] Dimethylhalogenonium ion salts were observed when a slight excess of a methyl halide, other than the fluoride, was introduced into a cold superacid solution.[6]

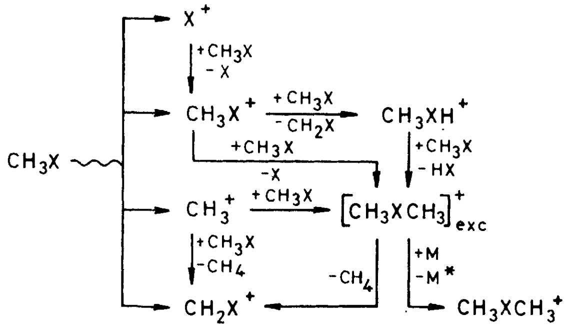
Careful investigations [4-7] on the mechanism of their formation led to the conclusions that the first formed donor–acceptor complex (I) undergoes an extensive nucleophilic displacement reaction by the nucleophile(s) Nu present, with formation of the alkylated intermediates (II), in particular a dimethylhalogenonium ion

$$CH_3X + MeX_n \longrightarrow \underset{\text{(I)}}{[CH_3X{\cdot}MeX_n]} \qquad (1)$$

$$Nu + [CH_3X{\cdot}MeX_n] \longrightarrow \underset{\text{(II)}}{[NuCH_3{}^{+}{\vdots}MeX^{-}{}_{n+1}]} \qquad (2)$$

salt, when the nucleophile is the methyl halide itself. Dimethylfluoronium ion salts cannot be prepared by this method, because when $X = F$ and $Nu = CH_3F$ (alone, or in $SO_2F_2$), a sort of ' internal solvation ' in the tightly bound donor–acceptor complex (I) prevents step (2), owing to the lack of nucleophiles stronger than $MeX^{-}{}_{n+1}$. Thus, it has been reported [4,8] that, both in neat $SbF_5$ and in $SbF_5{\cdot}SO_2F_2$ solutions, the $CH_3F{\cdot}SbF_5$ adduct represents the most powerful methylating agent known in the condensed phase; very recently, this claim has been challenged by Cacace and Giacomello,[9] who generated in the liquid phase a *free* methyl cation from the β-decay of multitritiated methanes.

The failure to observe $CH_3FCH_3{}^+$ ions in superacidic solutions does not necessarily indicate a lack of thermodynamic stability for these species. Indeed, stable long lived $CH_3XCH_3{}^+$ ($X$ = F, Cl, Br, or I) ions have been readily generated in the gas phase from electron impact on neutral $CH_3X$ over a wide range of electron energy and total pressure,[10] and their formation mechanism elucidated using ion cyclotron resonance (i.c.r.) mass spectrometric techniques.[10g] The ion chemistry of the primary ions of methyl halides is summarized in Scheme 1.



SCHEME 1

Each elementary step of the network occurs at high rate, indicating that only a few collisions between the ionic species and the parent molecule are sufficient to generate the final stable ions, namely $CH_3XCH_3{}^+$ and $CH_2X^+$, whose unreactivity towards $CH_3X$ has been demonstrated under widely different experimental conditions.[10]

At atmospheric pressures, under the action of ionizing radiation [10p,11] methyl halides produce the same primary ionic species observed by mass spectrometric techniques, which readily react with the parent molecules forming $CH_3XCH_3^+$ and $CH_2X^+$ ions, whose relative abundance is however unpredictable on the grounds of low-pressure data.

The present report is directed to determining the relative yields of dimethylhalogenonium ($CH_3XCH_3^+$) and halogenomethylium ($CH_2X^+$) ions, when generated in methyl halides at atmospheric pressures, and to compare their gas-phase reactivity with those observed in the corresponding Friedel–Crafts systems.

## EXPERIMENTAL

*Materials.*—Methyl halides, oxygen, and ammonia were high purity gases from Matheson Co., used without further purification. A sample of reagent grade benzyl fluoride was obtained from ICN Pharmaceutical Inc. Merck Co. provided all the other reagent grade chemicals and the reference compounds used in the g.l.c. analyses. Ethyl methyl ether was prepared from sodium ethoxide and dimethyl sulphate. Samples of 1,3,5-tri-t-butylbenzene and 3,5-di-t-butyltoluene were a kind gift from Professor F. Stegel; 2,4,6-tri-t-butyltoluene and isomeric t-butyltoluenes were prepared according to already reported procedures.[12] The starting materials were g.l.c. standards containing no detectable traces of the possible products of the methylation, halogenomethylation, ethylation, and halogenation reactions, as checked by g.l.c. on the same columns used in the final analyses.

*Samples Preparation.*—Pyrex bulbs (1 l), connected to a greaseless vacuum line, were outgassed and evacuated to $10^{-5}$ Torr, then filled with variable amounts of $CH_3X$ (X = F, Cl, Br; pressure ranging from 100 to 760 Torr), $O_2$ (2—4 Torr) as a thermal radical scavenger, the organic substrate(s) (1—2 Torr), and a gaseous base ($NH_3$), when required.

*Irradiations.*—The gaseous mixtures were irradiated with the $^{60}Co$ $\gamma$-rays in a 220 Gammacell (Atomic Energy Canada, Ltd.) at 37.5 °C, at a constant dose rate of 0.4 Mrad $h^{-1}$. After receiving a constant dose of a 4.8 Mrad, as determined with a Fricke dosimeter, portions of the samples were monitored by g.l.c. techniques.

*Products Analysis.*—The irradiated mixtures were analysed on a Hewlett–Packard model 5700 A gas chromatograph, equipped with a flame ionization detection unit. The products were identified by comparison of their retention volumes on at least two different columns with those of authentic samples, and their yields were determined from the area of the correspondent elution peaks using individual calibration factors.

*Ion Cyclotron Resonance Mass Spectrometric Experiments.*—I.c.r. experiments were performed by bombarding with 16 eV electrons, emitted by a heated rhenium filament, a 5 : 1 $CH_3X$–benzene mixture in the source region of the cell of a modified Varian Associates ion cyclotron mass spectrometer (Syrotron).

## RESULTS

Table 1 reports the $G_M$ values of the products M from the $\gamma$-radiolysis of $CH_3X$–benzene mixtures as a function of the molar fraction of added ammonia ($X_{NH_3}$), at constant total pressure. Product distributions and competition results, measured at variable $CH_3X$ pressures and in the presence of selected additives, are shown in Tables 2 and 3, respectively. The figures given were obtained at a constant dose of 4.8 Mrad (dose rate 0.4 Mrad $h^{-1}$) and represent the mean values from several irradiations carried out under the same conditions. The standard deviation is of the order of 10%, except for the lowest values, characterized by somewhat lower precision.

Analysis of Table 1 indicates that the distribution and yields of products depend greatly on the nature of the halogenomethane used as the bulk gas. Thus, $CH_3F$ systems are characterized by the formation of high yields of toluene and appreciable quantities of ethylbenzene and benzylamine (in the presence of ammonia). On the contrary, only low yields of toluene were recovered in $CH_3Cl$ and $CH_3Br$ systems, whereas ethylbenzene and benzylamine could not even be detected.

TABLE 1

Products yields in the $\gamma$-radiolysis of halogenomethane–benzene gaseous mixtures

| System composition [a] | | | Product yields $10^2$ $G_M$ [b] | | | | |
|---|---|---|---|---|---|---|---|
| X | $CH_3X$ (Torr) | $NH_3$ (Torr) | $PhCH_3$ | $PhC_2H_5$ | $PhCH_2X$ | $PhCH_2NH_2$ | PhX |
| F | 760 | | 104.9 | 3.97 | n.d. [c] | n.d. | n.d. |
| F | 760 | 0.7 | 103.9 | 2.19 | 1.82 | 0.30 | n.d. |
| F | 760 | 1.3 | 78.5 | 2.40 | 1.82 | 0.23 | n.d. |
| F | 760 | 2.0 | 72.8 | 2.10 | 2.30 | 0.23 | n.d. |
| F | 760 | 5.0 | 38.2 | 0.10 | 2.27 | 0.26 | n.d. |
| F | 750 | 10.0 | 24.9 | 0.13 | 2.87 | 0.29 | n.d. |
| F | 743 | 17.0 | 23.1 | 0.09 | 2.51 | 0.12 | n.d. |
| F | 735 | 25.0 | 21.6 | 0.06 | 1.73 | n.d. | n.d. |
| Cl | 760 | | 0.58 | n.d. | 2.45 | n.d. | 0.87 |
| Cl | 760 | 1.0 | 0.40 | n.d. | 2.77 | n.d. | 0.80 |
| Cl | 760 | 2.0 | 0.20 | n.d. | 3.01 | n.d. | 0.78 |
| Cl | 760 | 5.0 | 0.48 | n.d. | 1.38 | n.d. | 0.75 |
| Cl | 750 | 10.0 | 0.83 | n.d. | 0.27 | n.d. | 0.65 |
| Cl | 735 | 25.0 | 0.96 | n.d. | 0.29 | n.d. | 0.18 |
| Br | 760 | | 0.05 | n.d. | 0.21 | n.d. | 0.31 |
| Br | 760 | 2.0 | 0.03 | n.d. | 0.11 | n.d. | 0.39 |
| Br | 760 | 5.0 | 0.06 | n.d. | 0.08 | n.d. | 0.36 |
| Br | 743 | 17.0 | 0.11 | n.d. | n.d. | n.d. | 0.51 |
| Br | 735 | 25.0 | 0.18 | n.d. | n.d. | n.d. | 0.50 |

[a] $O_2$ 4 Torr, benzene 1—2 Torr. Radiation dose 4.8 Mrad. [b] $G_M$ is the number of molecules M produced per 100 eV of absorbed energy. Standard deviation of data *ca.* 10%. [c] n.d. = not detectable.

TABLE 2

Gas-phase alkylation reactions

| System composition[a] | | | | | |
|---|---|---|---|---|---|
| $CH_3X$ | | $O_2$ (Torr) | $NH_3$ (Torr) | Substate(s) (Torr) | Product distribution (%)[b] |
| X | Torr | | | | |
| Br | 760 | 4 | 3 | MeOH (6.2) | MeOMe (100) |
| Cl | 760 | 4 | 3 | MeOH (5.2) | MeOMe (100) |
| F | 760 | 4 | 3 | MeOH (6.3) | MeOMe (98.8); MeOEt (1.2) |
| Br | 760 | 4 | | Benzene (1.6) | Toluene (8.8); benzyl bromide (36.8); bromobenzene (54.4) |
| Cl | 760 | 4 | | Benzene (1.5) | Toluene (14.9); benzyl chloride (62.8); chlorobenzene (22.3) |
| F | 760 | 4 | | Benzene (1.6) | Toluene (96.3); ethylbenzene (3.7) |
| F | 300 | 4 | | Benzene (1.1) | Toluene (89.2); ethylbenzene (10.8) |
| F | 100 | 4 | | Benzene (0.9) | Toluene (88.6); ethylbenzene (11.4) |
| Cl | 760 | 4 | | Toluene (1.9) | Xylyl chlorides (*o* 43.8; *m* 11.0; *p* 24.0); benzyl chloride (21.1) |
| F | 760 | 4 | 4 | Toluene (1.2) | Xylenes (*o* 51.1; *m* 22.3; *p* 26.6) |
| F | 760 | 4 | | Toluene (1.6) | Xylenes (*o* 50.7; *m* 20.0; *p* 25.3); ethyltoluenes (*o* 0.5; *m* 1.0; *p* 2.5) |
| F | 300 | 4 | | Toluene (1.7) | Xylenes (*o* 49.7; *m* 20.2; *p* 19.0); ethyltoluenes (*o* 1.7; *m* 2.5; *p* 6.3) |
| F | 100 | 2 | | Toluene (1.0) | Xylenes (*o* 49.0; *m* 20.1; *p* 18.7); ethyltoluenes (*o* 1.7; *m* 3.0; *p* 7.5) |
| F | 760 | 4 | 4 | *o*-Xylene (1.8) | Trimethylbenzenes (1,2,3 52.8; 1,2,4 47.2) |
| F | 760 | 4 | | *o*-Xylene (2.2) | Trimethylbenzenes (1,2,3 62.0; 1,2,4 38.0) |
| F | 300 | 2 | | *o*-Xylene (1.0) | Trimethylbenzenes (1,2,3 51.0; 1,2,4 49.0) |
| F | 100 | 2 | | *o*-Xylene (0.5) | Trimethylbenzenes (1,2,3 40.0; 1,2,4 60.0) |
| F | 760 | 4 | 4 | *m*-Xylene (2.2) | Trimethylbenzenes (1,2,3 27.2; 1,2,4 64.8; 1,3,5 8.0) |
| F | 300 | 4 | | *m*-Xylene (2.0) | Trimethylbenzenes (1,2,3 32.6; 1,2,4 60.7; 1,3,5 6.7) |
| F | 300 | 2 | | *m*-Xylene (1.1) | Trimethylbenzenes (1,2,3 30.0; 1,2,4 64.9; 1,3,5 5.2) |
| F | 100 | 2 | | *m*-Xylene (0.6) | Trimethylbenzenes (1,2,3 28.0; 1,2,4 65.7; 1,3,5 6.2) |
| F | 760 | 4 | 4 | *p*-Xylene (2.0) | Trimethylbenzenes (1,2,4 100) |
| F | 760 | 4 | | *p*-Xylene (2.0) | Trimethylbenzenes (1,2,4 100) |
| F | 300 | 2 | | *p*-Xylene (1.1) | Trimethylbenzenes (1,2,4 100) |
| F | 100 | 2 | | *p*-Xylene (0.8) | Trimethylbenzenes (1,2,4 100) |
| F | 760 | 4 | 2 | Mesitylene (2.2) | Tetramethylbenzenes (1,2,3,5 100) |
| F | 760 | 4 | | t-Butylbenzene (1.0) | Toluene (4.8); t-butyltoluenes (*o* trace; *m* 39.1; *p* 56.1) |
| F | 760 | 4 | 2 | 1,3,5-Tri-t-butylbenzene (0.1) | 3.5-Di-t-butyltoluene (trace); 2,4,6-tri-t-butyltoluene (n.d.) |

[a] Radiation dose 4.8 Mrad (dose rate 0.4 Mrad $h^{-1}$). [b] The absence of products different from those listed in the Table does not necessarily mean that they are not formed.

Small yields of chloro- and bromo-benzene are formed in the corresponding irradiated systems. while radiolysis of $CH_3F$–benzene mixtures does not generate fluorobenzene at all.[*] The only unifying aspect is the formation of benzyl halides, whose yields depend on $X_{NH_3}$. Figure 1 shows the effect of the ammonia concentration on the $G_M$ values of the products from the $CH_3F$–benzene mixtures.

The trend of the benzylamine yields as a function of $X_{NH_3}$ mimics that of benzyl fluoride except at high concentrations of $NH_3$ ($X_{NH_3}$ $3.25 \times 10^{-2}$), where significant yields of benzyl fluoride are still formed, whilst the reaction channel leading to benzylamine is completely blocked.

Apart from the influence of the added base, the nature of the halogen plays a prominent role among the factors governing the halogenomethylation yields. In fact, as shown in Figure 2, the effect of the added base on the benzyl halide *G* values changes with the specific halogen atom involved.

Regardless of the nature of the substrate, methylation is always the prevailing reaction pathway in the $CH_3F$ systems (Tables 1 and 2), whereas, in the irradiated $CH_3Cl$ and $CH_3Br$ gaseous mixtures, its extent depends on the nature of the substrate. *n*-Type centres [10p,†] react easily with $CH_3ClCH_3^+$ and $CH_3BrCH_3^+$ ions, which, on the contrary, seem rather unreactive toward the aromatic ring.

TABLE 3

Methylation reaction rate constant ratios [a]

| | |
|---|---|
| $CH_3OH$ | 3.40,[b] 707,[c] $2.5 \times 10^{5}$ [d] |
| Benzene | 1.00 [e] |
| Toluene | 0.66 [f] |
| *o*-Xylene | 0.75 |
| *m*-Xylene | 1.54 |
| *p*-Xylene | 1.14 |
| Mesitylene | 1.16 |
| t-Butylbenzene | $2.3 \times 10^{-2}$ [f] |
| 1,3,5-Tri-t-butylbenzene | $8 \times 10^{-4}$ |

[a] Competiton experiments performed at a radiation dose of 4.8 Mrad (dose rate 0.4 Mrad $h^{-1}$). [b] $CH_3FCH_3^+$ ion. [c] $CH_3ClCH_3^+$ ion. [d] $CH_3BrCH_3^+$ ion. [e] Benzene used as a reference substrate. [f] Calculated using mesitylene as a reference substrate.

The isomer distribution of the alkylated products (Table

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[*] Free radicals ($CH_2X$, $CH_3$, H) originating either by electron impact on $CH_3X$ or as by-products of the ion–molecule reactions of Scheme 1, are efficiently trapped by the added oxygen which however slowly combines with halogen atoms (J. E. Nicholas and R. G. W. Norrish, *Proc. Roy. Soc.*, 1968, **A307**, 391), producing species which can eventually act as halogenating agents. Halogen atoms are reactive species, whose tendency to abstract a hydrogen from $CH_3X$ decreases in the order $F > Cl > Br$ (J. W. T. Spinks and R. J. Woods, 'An Introduction to Radiation Chemistry,' Wiley, New York, 1964; J. E. Wilson, 'Radiation Chemistry of Monomers, Polymers, and Plastics,' Dekker, New York, 1974). It follows that appreciable concentrations of both free halogen atoms and other halogenating species ($XO_2$) are likely to be formed during the γ-radiolysis of $CH_3Cl$ and $CH_3Br$, accounting for the low yields of monohalogenated substrates observed in the mixtures, while the small quantities of F atoms formed in $CH_3F$ are readily captured by the $CH_3F$ molecules themselves.

[†] An extensive methylation of $NH_3$, from the attack of dimethylhalogenonium ions, has been recently observed at atmospheric pressure, M. Colosimo and R. Bucci, *J. Phys. Chem.*, in the press.

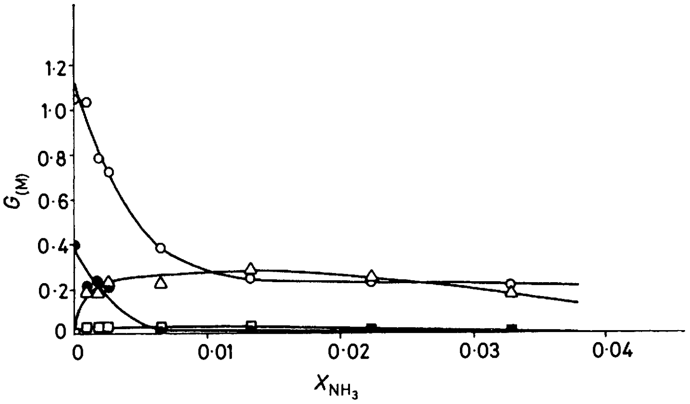


FIGURE 1 System, $CH_3F$ + benzene + $O_2$ + $NH_3$. Dependence of $G_M$ values on the molar fraction of ammonia ($X_{NH_3}$) for toluene (○); ethylbenzene (×10) (●); benzyl fluoride (△) (×10); and benzylamine (×10) (□)

2) and the competition experiments (Table 3) reflect the electrophilic nature of the alkylating species, whose ionic character is demonstrated by the drastic decrease of the alkylation yields following addition of limited concentrations of a base that intercepts the electrophile (Table 1). The dependence of the isomer distribution on the total pressure of the systems reveals the occurrence of isomerization toward the thermodynamically most stable isomer(s), which become(s) significant at low pressures.

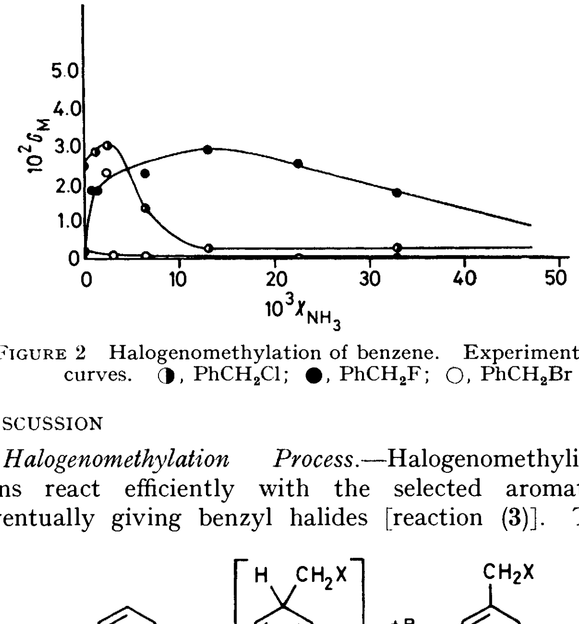
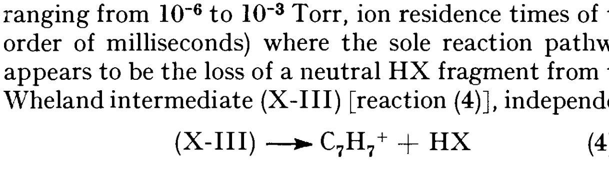


FIGURE 2 Halogenomethylation of benzene. Experimental curves. ◑, $PhCH_2Cl$; ●, $PhCH_2F$; ○, $PhCH_2Br$

## DISCUSSION



(3)

*Halogenomethylation Process.*—Halogenomethylium ions react efficiently with the selected aromatics eventually giving benzyl halides [reaction (3)]. The features of the gas-phase electrophilic attack of $CH_2X^+$ ions on aromatic molecules have been recently examined by i.c.r. techniques,[10c,13] under conditions (pressure ranging from $10^{-6}$ to $10^{-3}$ Torr, ion residence times of the order of milliseconds) where the sole reaction pathway appears to be the loss of a neutral HX fragment from the Wheland intermediate (X-III) [reaction (4)], independent of the nature of the halogen involved. Detailed inspections [13,14] of the ionic fluoromethylation of aromatic compounds carried out with the aid of deuteriated molecules revealed that the fluoromethylated σ-complex (F-III), generated by the attack of $CH_2F^+$ ions on fully deuteriated benzene, undergoes 100% elimination of DF, while HF is the sole neutral fragment arising from the unimolecular dissociation of the fluorinated intermediates formed from the condensation between a deuteriated phenylium ion and $CH_3F$. These results indicate that the unimolecular dissociation of the arenium ion (F-III) is a fast process occurring prior to any appreciable H–D scrambling and involving exclusively the F atom and a ring hydrogen.

$$\text{(X-III)} \longrightarrow C_7H_7^+ + HX \qquad (4)$$

The relatively high tendency of (F-III), excited by the exothermicity of its formation, to eliminate HF and the isolation, in the irradiated $CH_3F$–$NH_3$–benzene mixtures, of minute, but appreciable amounts of benzylamine suggest that, even under high pressure conditions, process (4) occurs to a significant extent, involving the intermediacy of a benzyl cation, which is known to condense readily with $NH_3$ producing benzylamine.[15]

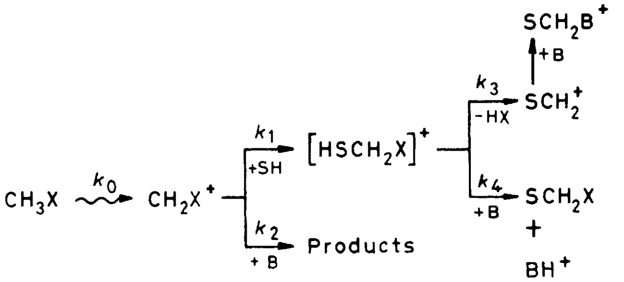
In conclusion, the products distribution, from the irradiated $CH_3F$ mixtures, and its dependence on $X_{NH_3}$ indicate that the (F-III) intermediate is likely to undergo two competitive processes, (i) unimolecular dissociation leading to a benzyl cation and (ii) loss of a proton to a base, with formation of neutral benzyl fluoride. However, the significant yields of benzyl chloride and bromide, even in the mixtures containing no added $NH_3$, denote the high stabilities of the relative σ-complexes, when compared with that of (F-III).

The proposed halogenomethylation pattern is represented in Scheme 2 where SH is the aromatic substrate and B is a base.

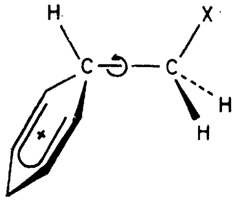
Kinetic treatment of the halogenomethylation reaction network, by application of the steady-state approximation, shows that, at a constant dose rate and substrate concentration, $[SCH_2X]$ is dependent only on [B].

The following points are also significant. (i) The experimental trend of the halogenomethylation yields are in agreement with the proposed general reaction pattern. (ii) The $G(CH_2X^+)$ values increase in the order

Br $\ll$ Cl < F, in accord with the bond dissociation energies [$D(CH_3$–Br) < $D(CH_3$–Cl) < $D(CH_2X$–H) < $D(CH_3$–F)] of methyl halides, which favour the formation of $CH_3^+$ ions by irradiating $CH_3Br$ and $CH_3Cl$ mixtures, whereas $CH_2F^+$ ions are preferentially formed in $CH_3F$.[16] (iii) In the fluoromethylation of benzene, the rate of the proton transfer (3) is comparable to the rate of the unimolecular dissociation (4), but it becomes predominant upon increasing $X_{NH_3}$. (iv) On the other hand, in the chloro- and bromo-methylation processes, deprotonation is fast, even in the absence of an added base.[*] Moreover, the (Br-III) complex is sufficiently stable that the only significant reaction channel is the proton transfer process (3). Consequently, the intrinsic stabilities of (X-III) appear to increase in the order Br > Cl $\gg$ F.[†]



SCHEME 2



(X-III)

A rationale for the diverse stabilities of (X-III) may be found in the conformational barriers associated with the $C_{ring}$–$C_\alpha$ bond rotation. The ease of interconversion may play a significant role in the establishment of an effective interaction between the ring hydrogen,[13] and the halogen atom, preliminary to the unimolecular decomposition of (X-III).[‡]

*Methylation Reaction*.—The methyl cation affinities (m.c.a.) [10g] of methyl halides, benzene, methanol, and ammonia are listed in Table 4. Methylation by dimethylhalogenonium ions of all the selected substrates is an exothermic and therefore energetically allowed process. Indeed, attack of $CH_3XCH_3^+$ ions on n-bases, such as $CH_3OH$ and $NH_3$ [10p] gives rise to considerable yields of methylated products. However, an evident discord between the exothermicity of $CH_3XCH_3^+$ attack on the arenes and the observed methylation yields exists.

TABLE 4

Methyl cation affinities of various species [a]

| Species | M.c.a./kcal mol$^{-1}$ | Reference |
|---|---|---|
| $CH_3F$ | 44 ± 8 | 10g |
| $CH_3Cl$ | $\geqslant$51 | 10g |
| $CH_3Br$ | $\geqslant$53 | 10g |
| Benzene | 88 | b |
| $CH_3OH$ | 82 | c |
| $NH_3$ | 102 | d |

[a] Methyl cation affinities (m.c.a.) as defined in ref. 10*g*. [b] Calculated using $\Delta H_f^\circ$ 193 kcal mol$^{-1}$, for the *ipso*-protonated toluene (J. L. Devlin, III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1976, **98**, 1990. [c] Calculated using $\Delta H_f^\circ$ ($CH_3OH$) −48 and $\Delta H_f^\circ$ ($CH_3OCH_3$) −44 kcal mol$^{-1}$ (D. H. Stull, E. F. Westrum, jun., and G. C. Sinke, 'The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969), and a proton affinity of 190 kcal mol$^{-1}$ for $CH_3OCH_3$ (R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, 1976, **98**, 1320. [d] Calculated using $\Delta H_f^\circ$ ($CH_3NH_2$) 5.5 and $\Delta H_f^\circ$ ($NH_3$) −11 kcal mol$^{-1}$ and a proton affinity for $CH_3NH_2$ of 211 kcal mol$^{-1}$ (M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 1969, **73**, 4328.

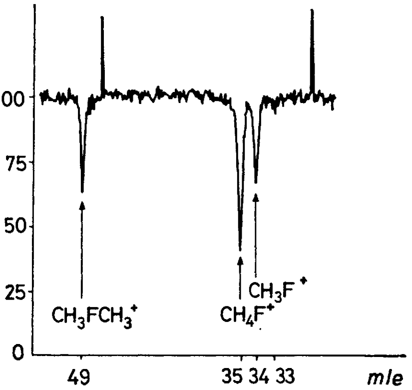


FIGURE 3 Double-resonance spectrum of *m/e* 93 in $CH_3F$–benzene

It might be argued that the diverse reactivity displayed by dimethylhalogenonium ions towards arenes can be ascribed to their degree of clustering from $CH_3X$, resulting in a parallel alteration of their electrophilic properties. But, i.c.r. experiments directed to assess the reactivity of $CH_3XCH_3^+$ ions towards benzene at pressures sufficiently low to prevent clustering, proved the consistency between the reactivity of naked $CH_3XCH_3^+$ ions towards benzene and that observed under radiolytic conditions. Indeed, as illustrated in Figure 3, i.c.r. double resonance experiments established a clear-cut relationship between $C_7H_9^+$, *m/e* 93, ions and their parent $CH_3F^+$, *m/e* 34, $CH_4F^+$, *m/e* 35, and $C_2H_6F^+$, *m/e* 49, ions, in $CH_3F$ systems, while the precursors of

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[*] As a matter of fact, γ-radiolysis of the components of the gaseous mixtures always generated basic products which, together with those from the glass walls of the bulb, can be considered as a source of a constant, small concentration of base.

[†] This conclusion would not be any longer correct if the $k_4$ values are very different for differently halogenated σ-complexes. The rate constants of the proton transfers to $NH_3$ from a number of protonated compounds have been measured by means of different experimental techniques. At 297 K and total pressures ranging from 0.2 to 2.0 Torr, *i.e.* under conditions resembling as closely as possible those of the present experiments, the measured values always range from $1 \times 10^{-9}$ to $5 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (R. E. Hemsworth, J. D. Payzant, H. I. Schiff, and D. K. Bohme, *Chem. Phys. Letters*, 1974, **26**, 417).

[‡] The fast unimolecular dissociation of fluorinated (III) finds interesting analogies with the i.c.r. results of Ridge and Beauchamp (*J. Amer. Chem. Soc.*, 1971, **93**, 5925), who demonstrated the occurrence, and the chemical consequences of strong hydrogen bonding involving gaseous Brønsted acids and fluorinated substrates.

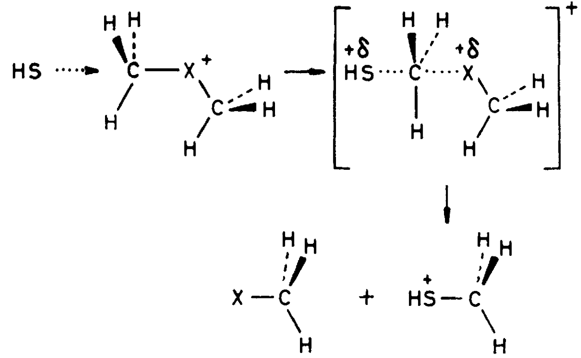
$C_7H_9^+$ ions, formed in $CH_3X$ (X = Cl or Br)–benzene mixtures, were found to be exclusively $CH_3X^+$ and $CH_4X^+$. Therefore, we are inclined to exclude, in the present case, a correlation between the degree of clustering of the methylating ions and their discriminating behaviour towards arenes, but rather the observed reactivity trend appears to be linked to the intrinsic electronic and structural features of the $CH_3XCH_3^+$ ion. Indeed, a strict dependence of the alkylating ability of open-chain dialkylhalogenonium ions on their structural parameters has been already demonstrated in solution studies.[5]

Recent semiempirical calculations,[10l] confirmed by $^1H$ and $^{13}C$ n.m.r., laser Raman, and i.r. spectroscopic studies,[4] assign a $C_{2v}$ bent conformation to the $CH_3XCH_3^+$ ions, with C–X–C bond angles ranging from 108° 50′ (X = I or Br) to $\geqslant 125°$ (X = Cl).*

The distortion of the bond angle in $CH_3ClCH_3^+$ has been attributed to some degree of charge delocalization from the chlorine atom to the methyl groups, which results in an increased $sp^2$ hybridization of their carbon atoms. Unfortunately, neither theoretical calculation nor spectroscopic information on the structural parameters of the $CH_3FCH_3^+$ ion are available. Nevertheless, owing to the scarce overall donor ability of fluorine, when adjacent to a $C^+$ centre,[17] it is plausible that, in the $CH_3XCH_3^+$ series, dimethylfluoronium ion possesses the highest degree of charge delocalization and, therefore, the carbon atoms have the maximum degree of $sp^2$ hybridization. As a consequence, the electronic and structural features of the methyl groups of $CH_3FCH_3^+$ are expected to be very similar to those typical of a planar carbenium ion.

In the light of recent information[18] on the stereochemical course of gas-phase nucleophilic displacement processes on selected open-chain halogenonium ions, the methylation of the substrate HS by attack of $CH_3XCH_3^+$ ions can be regarded as proceeding by the nucleophilic attack of the substrate itself on the methyl group of the dimethylhalogenonium ion, involving inversion of configuration of the carbon atom undergoing the attack.[5,10p,18] The activation energy of this process decreases as the $sp^2$ character of the $CH_3$ groups increases, as in the $CH_3FCH_3^+$ ions.† This view accounts for the observed high reactivity of dimethylfluoronium ions even towards non-localized nucleophilic centres, such as the π-system of the arenes. On the other hand, methylation of aromatic substrates by $CH_3ClCH_3^+$ and $CH_3BrCH_3^+$ ions involves a much higher activation barrier on account of the distinct $sp^3$ character of the carbon centre and, therefore, only powerful nucleophiles, such as $CH_3OH$ and $NH_3$, can establish a proper interaction to overcome the methylation activation energy.

The rates of attack on arenes by dimethylhalogenonium ions are modified when the substrate is sterically hindered, as shown in Table **3**, where the lower reactivity of $CH_3FCH_3^+$ ions towards sterically encumbered substrates, such as 1,3,5-tri-t-butylbenzene and to a minor extent, t-butylbenzene and mesitylene, demonstrates that repulsive interactions between the methyl groups of the electrophile and the bulky substituent of the aromatic compound hinder the attack of even the most reactive dimethylhalogenonium ions studied.



The occurrence of a significant ethylation process in $CH_3F$ mixtures is an additional piece of evidence of the low stability of $CH_3FCH_3^+$ ions; its inherent tendency to isomerize slowly to the more stable structure of protonated ethyl fluoride‡ is suggested by an appreciable effect of the total pressure on the relative extent of the ethylation process (Table 2). An increase of the $CH_3F$ pressure favours the collisional thermalization of the activated $CH_3FCH_3^+$ ions at the expense of any competitive isomerization process.

*Positional Selectivity*.—The isomer distributions of the products from the alkylation reactions on the selected aromatic compounds are reported in Table 2. The products composition underlines the electrophilic nature of all the alkylating agents, which preferentially attack the most nucleophilic positions of the aromatic substrate.[19] For instance, methylation of toluene occurs more in the *ortho*- and *para*-positions, while only relatively small amounts of *m*-xylene are formed. However, the primary xylenium ions tend to isomerize into the thermodynamically more stable 1,3-dimethylbenzenium ion structure, as apparent when the reaction is carried out at the lowest pressure used and in the absence of added bases, *i.e.* under conditions allowing isomerization. At higher $CH_3F$ pressures, collisional deactivation of the arenium ions predominates over the competitive intramolecular alkyl shifts, as indicated by the essentially constant *para* : 0.5 *meta* ratios of toluene in an extensive pressure range (Table **6**).

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* Extended Hückel theory [10l] anticipated a *ca.* 125° bond angle value for $CH_3ClCH_3^+$ while more recent MINDO/3 and perturbation theory calculations assign 127.5° to the $Pr^iClH^+$ bond angle, W. Jorgensen, *J. Amer. Chem. Soc.*, 1977, **99**, 280.

† The opposite methylation trend (Br > Cl > F), observed for $CH_3OH$ and $NH_3$, can be ascribed to the different ion yields (F < Cl < Br), from the γ-radiolysis of the parent halogenomethanes, on account of their different ionization potentials ($CH_3F$, 12.85 eV; $CH_3Cl$, 11.25 eV; $CH_3Br$, 10.54 eV), V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, 'Bond Energies, Ionization Potentials, and Electron Affininities,' Arnold, London, 1966.

‡ $\Delta H_f°$ ($C_2H_5FH^+$) = 140 kcal mol$^{-1}$ using a proton affinity for $C_2H_5F$ of 163 kcal mol$^{-1}$, J. L. Beauchamp, 'Interaction between Ions and Molecules,' ed. P. Ausloos, Plenum, New York, 1975.

TABLE 5

Aromatic electrophilic attack by different gaseous ions

| | | | Relative yields of isomers from toluene [a] (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| Electrophile | $\Delta H_f°$/ kcal mol$^{-1}$ | $k_t/k_b$ ratio | *ortho* | *meta* | *para* | $\frac{\textit{para}}{0.5\ \textit{meta}}$ | $\frac{\textit{para}}{0.5\ \textit{orthio}}$ | Reference |
| $^3HeT^+$ | 323 | 2.1 ± 0.2 | 57.0 | 18.6 | 23.4 | 2.6 | 0.8 | 20*a* |
| $^{80}Br^+$ | 300 | 2 | 43.2 | 28.6 | 28.3 | 2.0 | 1.3 | 20*b* |
| $CT_3^+$ | 258—290 | 0.80 | 22.0 | 64.0 | 14.0 | 0.4 | 1.3 | 9 |
| $D_2T^+$ | 256 | 1.3 ± 0.1 | 52.2 | 15.9 | 31.9 | 4.1 | 1.2 | 20*c* |
| $CH_2Cl^+$ | 228 | 6.0 | 55.6 | 14.0 | 30.4 | 4.3 | 1.1 | This work |
| $C_2H_5^+$ | 225 | 0.81 | 43.5 | 34.5 | 22.0 | 1.3 | 1.0 | 20*l* |
| i-$C_3H_7^+$ | 192 | 0.6—0.9 | 35.5 | 27.2 | 37.2 | 2.7 | 2.1 | 20*d* |
| t-$C_4H_9^+$ | 167 | 54—57 | | 5.4 | 94.6 | 35.0 | ∞ | 20*f* |
| $CH_3FCH_3^+$ | 161 | 0.66 | 52.8 | 20.8 | 26.4 | 2.5 | 2.0 | This work |
| $CF_3^+$ | 99 | 0.38 | 4.2 | 30.5 | 65.3 | 4.3 | 31.1 | 20*g* |

[a] Only nuclear substitution taken into account.

*Comparison with Other Gas-phase and Solution Alkylations.*—The substrate and positional selectivity of $CH_3FCH_3^+$ ion is compared with those of other gaseous electrophiles (Table 5), and with those of Friedel–Crafts methylating agents (Table 6).

Apart from electrophiles formed by decay, such as $^3HeT^+$ and $CT_3^+$, which were generated in a large excess of the substrate(s) and whose reactivity cannot be therefore kinetically linked to those of gaseous ions studied in gases containing very low concentrations of arene(s), the ionic species listed in Table 5 display fairly different reactivity and selectivity features. The positional selectivity of most electrophiles listed appears to depend on complicated factors, as well as their substrate selectivity, characterized by values ranging over two orders of magnitude. Gaseous ionic species may give rise to at least three different pathways, (i) substitution, (ii) hydride-ion abstraction from the methyl group of toluene, and (iii) proton transfer to the substrate. The relative extent of each of these processes is largely dependent of the nature of the attacking electrophile, and the inter- and intra-molecular selectivity displayed in the substitution process must be therefore considered as the result of the superimposition of all the reaction channels. Moreover, in some cases, such as for t-$C_4H_9^+$ and, to a lesser extent, i-$C_3H_7^+$ ions, which display high *para* : 0.5 *ortho* values, an additional effect (steric hindrance) is also present.[20]

The reactivity properties of gaseous $CH_3FCH_3^+$ ions are similar to those of free carbenium ions (*e.g.* $C_2H_5^+$), suggesting that dialkylfluoronium ions can be compared to poorly solvated carbenium ions. On the other hand, $CH_3ClCH_3^+$ and $CH_3BrCH_3^+$ ions are members of a totally new class of gaseous electrophiles, whose reactivity and selectivity appear to depend, *inter alia*, on the energy barrier required for the inversion of configuration of their alkyl groups.

A comparison between the properties of gaseous dimethylfluoronium ions and those of the analogous Friedel–Crafts methylating agents ($CH_3F$–$SbF_5$ solutions; see Table 6) is convincing evidence that, apart from the effects due to the environment, the mechanisms operating in these systems are very similar. On the other hand, the scarce reactivity towards arenes, typical of $CH_3ClCH_3^+$ and $CH_3BrCH_3^+$ ions, does not match the alkylating ability displayed by the corresponding Friedel–Crafts intermediates. A possible explanation can be found in the effects of the different extent of solvation of both the alkylating species and the σ-complexes formed, which favours the methylation process in the condensed phase.

*Conclusions.*—The essential features of aromatic alkylation reactions occurring under Friedel–Crafts conditions are exhibited by the gas-phase electrophilic attack of $CH_3FCH_3^+$ ions, formed by γ-radiolysis of $CH_3F$, on selected arenes. The same conclusions cannot be drawn for the $CH_3ClCH_3^+$ and $CH_3BrCH_3^+$ ions, which are rather unreactive towards aromatic substrates. These

TABLE 6

Isomer distribution from the methylation of toluene

| System composition | | | | Isomer distribution (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| Methylating agent | Phase | Solvent | Temp. (°C) | *ortho* | *meta* | *para* | para : 0.5 meta ratio | Reference |
| $CH_3FCH_3^+$ | Gas (760 Torr) [a] | | 37.5 | 51.1 | 22.3 | 26.6 | 2.38 | This work |
| $CH_3FCH_3^+$ | Gas (760 Torr) [b] | | 37.5 | 52.8 | 20.8 | 26.4 | 2.54 | This work |
| $CH_3FCH_3^+$ | Gas (300 Torr) [b] | | 37.5 | 55.9 | 22.7 | 21.4 | 1.88 | This work |
| $CH_3FCH_3^+$ | Gas (100 Torr) [b] | | 37.5 | 55.8 | 22.9 | 21.3 | 1.86 | This work |
| $CT_3^+$ | Gas (72 Torr) [b] | | 90 | 22.0 | 64.0 | 14.0 | 0.44 | *c* |
| $CT_3^+$ | Liquid [b] | Toluene | 22 | 40.1 | 27.0 | 32.9 | 2.44 | *d* |
| $CH_3F$–$SbF_5$ | Liquid | $SO_2ClF$ | −78 | 53.6 | 18.5 | 27.9 | 3.02 | *e* |
| $CH_3F$–$SbF_5$ | Liquid | $SO_2ClF$ | 25 | 44.3 | 29.4 | 26.3 | 1.79 | *e* |
| $CH_3Cl$–$SbF_5$ | Liquid | $SO_2$ | −50 | 52.3 | 15.7 | 32.0 | 4.08 | *e* |
| $CH_3Br$–$SbF_5$ | Liquid | $SO_2$ | −50 | 57.8 | 9.5 | 32.7 | 6.88 | *e* |
| $CH_3Cl$–$AlCl_3$ | Liquid | $CH_3NO_2$ | 13 | 52 | 16 | 32 | 4.0 | *e* |
| $CH_3Br$–$AlBr_3$ | Liquid | | 0 | 54 | 17 | 29 | 3.4 | *e* |
| $CH_3I$–$AlBr_3$ | Liquid | | 0 | 48 | 12 | 40 | 6.7 | *e* |

[a] $NH_3$ 4 Torr. [b] No added base. [c] F. Cacace and P. Giacomello, *J.C.S. Perkin II*, 1978, 652. [d] F. Cacace and P. Giacomello, *J. Amer. Chem. Soc.*, 1977, **99**, 5477. [e] G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Amer. Chem. Soc.*, 1974, **96**, 884.

species sharply discriminate between $n$- and $\pi$-type basic centres, indicating that their reactivity is largely dominated by an activation barrier whose size is related to the degree of $sp^2$ hybridization associated with the carbon atoms of their methyl groups. A noticeable steric effect, which is in agreement with the presence of an energy barrier in these alkylation reactions, has been observed even for dialkylfluoronium ions attacking encumbered substrates, such as mesitylene, t-butylbenzene, and tri-t-butylbenzene.

Together with $CH_3XCH_3^+$ ions, other minor species, such as $CH_2X^+$ ions (F 4%; Cl 2%; Br 0.1%, of the total ion yield), are simultaneously formed in the $\gamma$-radiolysis of $CH_3F$. The attack of $CH_2X^+$ ions on benzene leads to Wheland intermediates, whose inherent stability towards their unimolecular dissociation with loss of HX, decreases in the order $Br > Cl \gg F$.

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