Gas-phase Methylation of Toluene by $CT_3YCH_3^+$ (Y = F, Cl, and Br) Ions †

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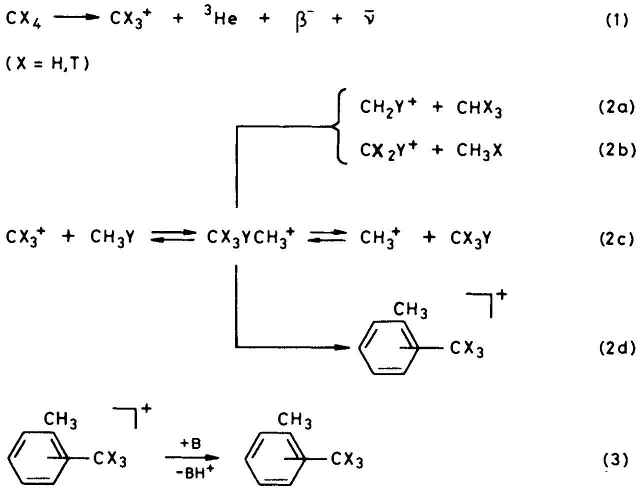
CX_3^+ ions (X = H, T), formed by the spontaneous β^- decay of CX_4, were allowed to react with gaseous CH_3Y (Y = F, Cl, and Br) in the presence of a trace amount of toluene. The formation of radioactive isomeric xylenes, arising from the attack of $CH_3YCH_3^+$ ion to C_7H_8, is discussed.

The importance of dimethylhalogenonium ions in Friedel–Crafts methylation reactions with methyl halides is well known [1] and these electrophiles are gaining interest also as potential gaseous methylating agents of synthetic utility.[2] They are reported to alkylate n bases easily,[2,3] but their low reactivity towards π systems was noted,[2b,4,5,‡] although other gaseous CH_3ZR^+ ions, *e.g.* Z = Br, R = cyclo-C_3H_5,[6] react with benzene and yield easily detectable condensation products.

Since we are able to generate tritium-labelled dimethylhalogenonium ions in the gas phase,[3,7] we report here the application of a very sensitive radiotracer method to study the reactions of $CT_3YCH_3^+$ ions (Y = F, Cl, and Br) with toluene in order to gain better insight into the course of the gas-phase methylation of arenes. This approach presents two advantages over similar studies: (i) it allows structural discrimination of the products, contrary to what happens in mass spectrometric experiments;[2,5] and (ii) its sensitivity can easily be made higher than that of radiolytic methods,[4] since it depends on the quantity of methylium ion precursors one wants to generate from CX_4 in the well defined nuclear decay process.

The reactions under investigation are (1)—(3). Reactions (1) [8,9] and (2a—c) [3,7,10-12] are established processes; reactions (2d) and (3) were observed in the gas phase only for Y = F and the methylating agent was produced from CH_3F by γ-radiolysis.[4]



Experimental

Materials.—Methyl fluoride and methyl chloride (Matheson), methyl bromide, toluene, and isomeric xylenes (Merck), and oxygen (SIO) were high purity products and used as received. When used, polytritiated methane, from a stock solution of CT_4 in CH_4,[13,§] had the following isotopic composition: CT_4, 37%; CHT_3, 32%; CH_2T_2, 18%; and CH_3T, 13%.[7,¶]

Sample Preparation.—Pyrex bulbs having a tube closed by a break-seal were filled with the desired gases on a vacuum line according to a procedure described in detail elsewhere.[3b,7] Toluene was contained in small Pyrex ampoules having fragile points, which were broken by shaking the sealed bulbs. The samples were stored at room temperature (*ca.* 300 K).

Analysis.—Each sample was tested as follows. After the storage time, inactive *o*-, *m*-, *p*-xylenes and a magnet were introduced into the Pyrex tube of the bulb. Afterwards, the tube was connected to a vacuum line by a greaseless joint and at atmospheric pressure the break-seal was broken by allowing the magnet, driven upwards inside the tube by another external magnet, to fall against the fragile point. The bulb was cooled to the liquid nitrogen temperature to condense the carrier isomeric xylenes (398 ± 5 µl each) into it. Afterwards, several freeze–thaw cycles were carried out to equilibrate the mixture composition. The uncondensed vapours were removed from the bulb by a Toepler pump in freeze–pump–thaw cycles at the temperature of freezing chloroform. At the end, the remaining liquid mixture of arenes, possibly containing traces of gases dissolved in it, was removed from the bulb by a syringe and transferred into a vial; the components were separated by preparative g.l.c. on a Bentone 34–dodecyl phthalate (8 : 10) column. The xylenes were assayed in a liquid scintillation counter. The g.l.c. purification procedure was repeated until a constant specific activity, *i.e.* disintegrations s^{-1} mg^{-1}, was reached. The inverse isotopic dilution method was applied.

Results

In Table 1 the experimental conditions and results are presented. Radioactive isomeric xylenes are formed in every system, and their yields are calculated as percentages of CX_3^+ ions which are formed by the nuclear decay of CX_4 and are found in the products; the ' blind ' reaction channel of CH_3^+ ions, generated by CH_3T and yielding unlabelled xylenes, is taken into account. The results are mean values of at least three independent samples, and at least ten scintill-

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‡ Dimethylfluoronium ion is an exception, see ref. 4.

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Table 1. $CX_4 + CH_3Y + PhCH_3$; X = H, T; Y = F, Cl, and Br

Y	$p(CH_3Y)$ (Torr)	Activity CX_4 (mCi l^{-1})	$p(O_2)$[a] (Torr)	$p(PhCH_3)$ (Torr)	V(l)	Decay time (day)	Radiochemical yield of xylenes[b] *o*	*m*	*p*
F	660	6.90	4	6	1.05	949	0.030	0.023	0.043
F	660	6.90	4	6	1.05	950	0.028	0.023	0.043
Cl	660	6.90	4	6	1.05	951	1.30	0.59	1.48
Cl	660	6.90	4	6	1.05	952	1.30	0.61	1.50
Br	660	6.90	4	6	1.05	953	1.32	0.71	1.23
Br	660	6.90	4	6	1.05	954	1.28	0.69	1.16

[a] Added as a thermal radical scavenger. [b] % of formed radioactive CX_3^+ ions

Table 2. Methylation of toluene in the gas-phase

System	Method	Process	Isomeric distribution of xylenes (%) *o*	*m*	*p*	*para* : ½ *meta*	*para* : ½ *ortho*	Ref.
$CT_4 + PhCH_3$	β^- Nuclear decay	$CT_3^+ + PhCH_3$	24	56	20	0.72	1.67	14
$CT_4 + PhCH_3$	β^- Nuclear decay	$CT_3^+ + PhCH_3$	24	56	18	0.62	1.50	15*a*
$CH_3F + PhCH_3$	γ-Radiolysis	$(CH_3)_2F^+ + PhCH_3$	53	56	26	2.54	0.98	4
$CH_3Cl + PhCH_3$	γ-Radiolysis	$(CH_3)_2Cl^+ + PhCH_3$	*a*	*a*	*a*			4
$CH_3Br + PhCH_3$	γ-Radiolysis	$(CH_3)_2Br^+ + PhCH_3$	*a*	*a*	*a*			4
$CH_3Cl + PhCH_3$	Electron impact	$(CH_3)_2Cl^+ + PhCH_3$	*b*	*b*	*b*			5
$CH_3NO_2 + PhCH_3$	Electron impact	$CH_3^+ + PhCH_3$	*c*	*c*	*c*			16
$CH_4 + CH_3Cl + PhCH_3$	Electron impact	$(CH_3)_2Cl^+ + PhCH_3$	*a*	*a*	*a*			2*b*
$CT_4 + CH_3F + PhCH_3$	β^- Nuclear decay	$(CH_3)_2F^+ + PhCH_3$	31	22	47	4.3	3.03	This work
$CT_4 + CH_3Cl + PhCH_3$	β^- Nuclear decay	$(CH_3)_2Cl^+ + PhCH_3$	38	18	45	5.0	2.37	This work
$CT_4 + CH_3Br + PhCH_3$	β^- Nuclear decay	$(CH_3)_2Br^+ + PhCH_3$	40	22	38	3.5	1.9	This work

[a] No formation noted. [b] $C_8H_{10}^+$ formation reported. [c] No addition of CH_3^+ ion to arenes reported, see text.

Table 3. Electrophilic attack by different gaseous ions to toluene

Electrophile	Isomeric distribution of xylenes (%) *o*	*m* Gas-phase	*p*	*para* : ½ *meta*	*para* : ½ *ortho*	Ref.
$^3HeT^+$	57	19	23	2.6	0.8	15*b*
$^{80}Br^+$	43	29	29	2.0	1.3	15*c*
D_2T^+	52	16	32	4.1	1.2	15*d*
CH_2Cl^+	56	14	30	4.3	1.1	4
$C_2H_5^+$	44	35	22	1.3	1.0	15*c*
iso-$C_3H_7^+$	36	27	37	2.7	2.1	15*f*
tert-C_4H_9	0	5	95	55.0	∞	15*g*
CF_3^+	4	31	65	4.3	32.5	17
CT_3^+	26	56	18	0.6	1.4	14
$CH_3FCH_3^+$	53	21	26	2.5	1.0	4
$CT_3FCH_3^+$	31	22	47	4.3	3.0	This work
$CT_3ClCH_3^+$	38	18	45	5.0	2.4	This work
$CT_3BrCH_3^+$	40	22	38	3.5	1.9	This work
		Liquid phase				
CT_3^+	40	27	33	2.4	1.7	15*h*
		Solid phase				
CT_3^+	48	28	24	1.7	1.0	18

ation countings, and are reproducible within the standard deviation of 15%. Under the conditions used the β^- decay irradiation dose is low, and the associated radiolytic phenomena are expected to be negligible with respect to the formation of the neutral products.

Table 2 collects the data relative to the studies of the gas-phase methylation of toluene; the *para* : 1/2 *meta* and *para* : 1/2 *ortho* ratios are reported as well.

In Table 3 the isomeric distribution obtained from the gas-phase reactions of several electrophiles E^+ and toluene are shown. It seems interesting to include also the results relative to CT_3^+ in the liquid- and solid-phase.

Discussion

The Formation of $CH_3YCH_3^+$ *Ions.*—Under the pressure conditions reported in Table 1 dimethylhalogenonium ions which are formed by CX_3^+ ions produced in equation (1) and survive the decomposition paths (2a—c),[3b,7] undergo several collisions with the parent methyl halides before being able to react with toluene. Thus, only thermal $CX_3YCH_3^+$ ions can participate in reaction (2d).

Methyl Cation Addition to Toluene.—The energetics of reaction (3) could be inferred from the methyl cation affinities (MCA) * of the unlabelled neutrals, if one neglects the effects deriving from H-T substitution. Table 4 lists the MCA values concerning the methyl halides of interest and benzene, as the only arene for which a reliable value is available.[19] Methyl cation transfer from methyl halides to benzene is allowed by thermochemistry, and indeed was observed.[4,6b] The difference among the MCA values of methyl halides and benzene is quite high and suggests that the class of arenes has MCA values higher than the class of halogenomethanes. In addition,

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* As in ref. 11, the methyl cation affinity of a molecule, *i.e.* MCA(S), is defined as $-\Delta H$ for $CH_3^+ + S \longrightarrow CH_3S^+$.

Table 4. Methyl cation affinities of various species

Species	MCA/kJ mol^{-1}	Reference
CH_3F	184	11*a*
CH_3Cl	213	11*b*
CH_3Br	222	11*b*
C_6H_6	368	19

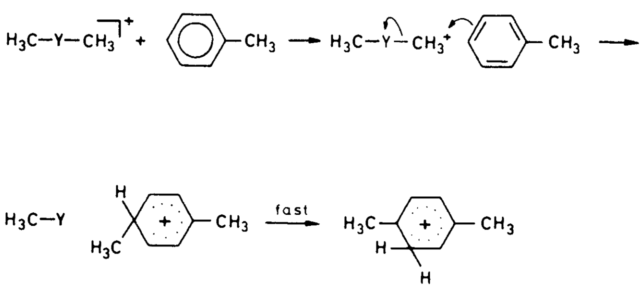
unambiguous and independent evidence has been gathered in recent years about the formation of xylenes and the condensation ions in the reactions of a number of methylating agents with C_7H_8 (see Table 2). The actual detection of isomeric C_8H_{10} compounds in all the systems investigated here proves that the methylation reactions of toluene with dimethylhalogenonium ions is thermodynamically allowed, and, consequently, the following order of MCA values holds: $C_7H_8 > CH_3Br \geqslant CH_3Cl > CH_3F$. The interference of direct reactions of free CX_3^+ ions with toluene can be disregarded, since free methylium ion always yields very different isomeric distributions,[14,15a,h,18] with which the present data bear no analogy. Also the interference of radical mechanisms can be ruled out because of the presence of oxygen, a good scavenger of thermal radicals.

Finally, the ability of electrophilic organic cations to condense with arenes in the gas phase has recently been challenged,[16,20] but our results do not support this alternative view.

The Influence of Halogen on the Formation of Xylenes.—The yields of thermal $CX_3YCH_3^+$ ions that survive the decomposition processes (2a—c) and react by (2d) are not known,[3] and the overall reactivity of toluene towards dimethylhalogenonium ions cannot be inferred directly from the radiochemical yields in Table 1. In fact, taking into account the halide ion transfer process (2c), caused by multiple, quasi-resonant, and almost thermoneutral methyl cation (labelled and unlabelled) exchange among the parent methyl halides,[3] and the methylation reactions of n bases with radiolytic dimethylhalogenonium ions,[4] one can infer that the population of stable $CX_3YCH_3^+$ ions as a function of Y is $F < Cl \leqslant Br$. Consequently, the radiochemical yields as functions of Y, *i.e.* $F < Cl \simeq Br$, obtained in this work reflect the difference in the number of stable methylating ions present in each halogenomethane system. It follows that the discrepancy with the reactivity order: $F \gg Cl \simeq Br$, determined in radiolytic experiments,[5] arises as an artifact of the methods used.

The isomeric distributions of xylenes produced in the present nuclear decay experiments underline the electrophilic character of the methylation reaction, according to which the most nucleophilic positions of the aromatic ring are attacked in preference.[21] Methylation of toluene always occurs in preference at the *ortho*- and *para*-positions, and only minor amounts of *meta*-xylene are formed. Primary xylenium ions tend to isomerize to the thermodynamically more stable 1,3-dimethylbenzenonium ions, unless collisional deactivation of the 1,2- and 1,4-dimethyl isomers occurs and prevents methyl group shifts. The Scheme outlines the mechanism of the formation of *para*-xylene.[2,4,22] Although depicted as linear, the C-Y-C angle increases as a function of Y in the order: $180° < F < Cl < Br < 108°$; at the same time, the sp^2 hybridization of the methyl group decreases when passing from Y = F to Cl to Br (ref. 4 and references therein).

Comparison with Other Gas-phase Electrophilic Agents.—In Table 3 the positional selectivity of $CX_3YCH_3^+$ ions is compared with those of other gaseous electrophiles. Apart from the differences existing among the nature and the structure of the ions and the methods to generate them, the reactivity of the electrophiles varies and is the superimposition of three paths, which depend largely on the nature and the structure of the ions themselves: (i) substitution; (ii) hydride-ion abstraction from the methyl group of toluene; and (iii) proton transfer to the arene. The overall effect may be responsible for the scatter of the observed *para* : 1/2 *meta* ratios. Also steric hindrance of the *ortho*-position is present, as evidenced by the *para* : 1/2 *ortho* ratios.[15] However, the reactivity of the $CX_3YCH_3^+$ ions generated by the nuclear method appears similar to that of D_2T^+, CH_2Cl^+, and CF_3^+ species, as far as the nucleophilic character of toluene is concerned, and to that of moderately encumbered ions, as far as the steric hindrance is considered.



Scheme.

Comparison with Condensed-phase Studies.—When comparing the present data with those obtained with analogous Friedel–Crafts methylating agents [1] the profound difference existing in the reaction environments must not be disregarded. However, the similarity of the mechanisms operating in the gas-phase and in superacid solutions is evident.

References

1 G. A. Olah, 'Halonium Ions,' Wiley, New York, 1975.
2 D. K. Sen Sharma and P. Kebarle, *J. Am. Chem. Soc.*, (*a*) 1978, **100**, 5828; (*b*) 1982, **104**, 19.
3 M. Colosimo and R. Bucci, *J. Phys. Chem.*, (*a*) 1979, **83**, 1952; (*b*) 1980, **84**, 3326.
4 M. Speranza, N. Pepe, and R. Cipollini, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1179.
5 J. A. Stone, M.-S. Lin, and J. Varah, *Can. J. Chem.*, 1981, **59**, 2412.
6 M. Colosimo and R. Bucci, (*a*) *J. Chem. Soc., Chem. Commun.*, 1981, 659; (*b*) *J. Chem. Soc., Perkin Trans. 2*, 1982, 461.
7 M. Colosimo and R. Bucci, *J. Phys. Chem.*, 1978, **82**, 2061.
8 A. M. Snell and F. Pleasonton, *J. Phys. Chem.*, 1958, **62**, 1337.
9 F. Cacace, (*a*) *Adv. Phys. Org. Chem.*, 1970, **8**, 79; (*b*) 'Interactions between Ions and Molecules,' ed. P. Ausloos, Plenum Press, London, 1975, p. 527.
10 N. A. McAskill, *Aust. J. Chem.*, (*a*) 1969, **22**, 2275; (*b*) 1970, **23**, 2301; (*c*) A. A. Herod, A. G. Harrison, and N. A. McAskill, *Can. J. Chem.*, 1971, **49**, 2217.
11 (*a*) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, 1972, **94**, 2788; (*b*) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *ibid.*, 1974, **96**, 1269.
12 J. M. S. Henis, M. D. Loberg, and M. J. Welch, *J. Am. Chem. Soc.*, 1974, **96**, 1665.
13 F. Cacace and M. Schuller, *J. Labelled Compd.*, 1975, **2**, 313.
14 V. D. Nefedov, E. N. Sinotova, G. P. Akulov, and M. V. Korsakov, *Zhur. Org. Khim.*, 1970, 6, 1214.
15 (*a*) F. Cacace and P. Giacomello, *J. Chem. Soc., Perkin Trans. 2*, 1978, 652; (*b*) F. Cacace and S. Caronna, *J. Am. Chem. Soc.*, 1967, **89**, 6848; (*c*) F. Cacace and G. Stocklin, *ibid.*, 1972, **94**, 2518; (*d*) F. Cacace, R. Cipollini, and G. Occhiucchi, *J. Chem. Soc., Perkin Trans. 2*, 1972, 84; (*e*) F. Cacace, R. Cipollini,

P. Giacomello, and E. Possagno, *Gazz. Chim. Ital.*, 1974, **104**, 977; (*f*) F. Cacace and E. Possagno, *J. Am. Chem. Soc.*, 1973, **95**, 3397; (*g*) F. Cacace and P. Giacomello, *ibid.*, 1973, **95**, 5851; (*h*) 1977, **99**, 5477.

16 J. D. Morrison, K. Stanney, and J. M. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 1981, 697.

17 R. Cipollini, G. Lilla, N. Pepe, and M. Speranza, *J. Phys Chem.*, 1978, **82**, 1207.

18 V. D. Nefedov, E. N. Sinotova, and V. A. Sciscikuno, *Zhur. Org. Khim.*, 1979, **15**, 1458.

19 MCA(C_6H_6) is calculated using ΔH_f 807 kJ mol^{-1} for the *ipso*-protonated toluene, J. L. Devin, III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, 1976, **98**, 1990.

20 J. D. Morrison, K. Stanney, and J. M. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 1981, 838.

21 F. M. Brower, E. L. Mackor, and C. McLean, 'Carbonium Ions,' eds. G. A. Olah and P. v. R. Schleyer, Wiley, New York, 1970, vol. II.

22 N. Pepe and M. Speranza, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1430.

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