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GAS PHASE ION CHEMISTRY :

A COMPARATIVE STUDY OF REACTION OF FIRST ROW TRANSITION METAL CATIONS WITH 2-METHYL PROPANE

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ABSTRACT : *The gas phase reactivity of first row transition metal cations with 2-methylpropane was investigated using a triple quadrupole mass spectrometer. This reactivity is very variable depending on the nature of the metal :* Ti^+ *and* V^+ *give mainly the multiple collision product* $M(C_8H_{14})^+$ *whereas* Cr^+, Mn^+, Cu^+ *and* Zn^+ *(reported to be unreactive under other conditions) add 1 or 2* C_4H_{10} *units ;* Fe^+, Co^+, Ni^+ *cleave C-H and C-C bonds of 2-methylpropane and react further.*

The gas-phase reactions of transition metal ions with hydrocarbons have been the subject of several recent investigations using ion cyclotron resonance (1-4), Fourier transform mass spectrometry (5-13), collision-activated decomposition spectroscopy (14,15) and ion beam techniques (16-22).
Most of these investigations focus on group 8 transition metals, while Mn^+, Cr^+ (20) and Cu^+ (23) are reported to be unreactive.

Using a prototype of triple quadrupole mass spectrometer (24) from the NERMAG company (25) we have compared the gas-phase reactivity of first row transition metal ions towards 2-methylpropane.

The metal ions, volatilized from a salt in a glycerol matrix using a FAB source (26), were selected by the first quadrupole and reacted in the collision chamber with the hydrocarbon at a pressure on the order of 10^{-3} torr. The resulting ions were then detected in the analyzer. The gas pressure and/or the length of the collision chamber are larger than in the above-mentioned techniques, allowing a large extent of conversion and the detection of multiple collision products. The collision energy is low : 0 to 1 eV in the center of mass frame.

Using these conditions, all the M^+ ions studied except K^+ (no reaction) and Ca^+ (very small cross-section, 1 $Å^2$) appeared to react with 2-methylpropane, with comparable cross-sections (10-100 $Å^2$). In all the cases where several isotopes of the metal are present with similar abundances, the reactions were carried out successively on all the isotopic ions and gave results in agreement with the proposed formula.

From Table it can be seen that the different metal ions exhibit clearly different reactivities towards 2-methylpropane. They can be roughly divided in three groups :

- Ti^+ and V^+ : the major reaction product is $M(C_8H_{14})^+$, corresponding to addition of 2 C_4H_{10} molecules and loss of 3 H_2. The relative abundances of the different products indicate that the primary product of the reaction between M^+ and 2-methylpropane is more reactive towards 2-methylpropane than the metal ion itself. Under ICR conditions (only primary reaction products), Ti^+ is known to dehydrogenate alkanes : with 2-methylpropane the major product is $Ti(C_4H_8)^+$ (3). It would be particularly interesting to know whether the observed multiple collision products involve the formation of new carbon-carbon bonds. Their structures are currently under investigation.

- Cr^+, Mn^+, Cu^+ and Zn^+ (d^5 and d^{10} ions) : the main reaction pathway is the neat addition of the hydrocarbon to the metal ion, giving $M(C_4H_{10})^+$. $Cr(C_4\ H_{10})^+$ was reported to be formed from $Cr(CO)^+$ and 2-methylpropane : its CAD spectrum suggests that the C_4H_{10} unit retains its integrity (2). Direct reaction of Cr^+ with 2-methylpropane under ICR conditions gives $Cr(C_4H_8)^+$, Mn^+ being unreactive (2). Both Mn^+ and Cr^+ are unreactive towards alkanes under ion beam conditions (20). Although a variety of $Mn(ligand)^+$ ions have been prepared by ligand exchange (27), no Mn $(alkane)^+$ complex had been reported yet.

In the case of Cr^+ and Cu^+ a second molecule of 2-methylpropane may react to give $M(C_4H_{10})_2{}^+$.

Formation of $C_4H_9{}^+$ is also observed : for Mn^+ and Zn^+ it is the major product. Preliminary studies indicate that in the case of Cu^+ the ratio of ion abundances $(C_4H_9{}^+)/(Cu(C_4H_{10})^+ + Cu(C_4H_{10})_2{}^+)$ increases with pressure, suggesting that $C_4H_9{}^+$ arises at least partially from a secondary reaction of $Cu(C_4H_{10})^+$ and/or $Cu(C_4H_{10})_2{}^+$.

- Fe^+, Co^+, Ni^+ : as expected from literature, group 8 metal ions are the most reactive, giving in particular $M(C_4H_8)^+$ and $M(C_3H_6)^+$ (1-3,7,14,16, 19-21). The abundance ratios $M(C_4H_8{}^+)/M(C_3H_6)^+$, decreasing from Fe to Ni, are in good agreement with those reported under ion beam conditions with a similar collision energy (20,21). The CAD spectrum of $Fe(C_4H_{10})^+$ obtained by reaction of $FeCO^+$ with 2-methylpropane also affords $Fe(C_3H_6)^+$ and $Fe(C_4H_8)^+$ in similar proportions (14).

Several products from multiple collisions are observed in addition, the major ones being $M(C_7H_{16})^+$ and, in the case of iron, $M(C_8H_{18})^+$. $M(C_4H_{12})^+$, important in the case of nickel, might have either a $M(CH_3)_4{}^+$ or an hydride structure.

Another important fragment, especially with nickel, is $C_4H_9{}^+$. Since direct hydride abstraction from 2-methylpropane by Ni^+ or Co^+ is an endothermic reaction observed only at high collision energy under ion beam conditions (16, 20), $C_4H_9{}^+$ might be a secondary reaction product.

For comparison, Ar^+, generated from non-neutralized Ar in the FAB beam, was

TABLE : Relative abundance (%) of the main ionic reaction products between different reacting ions M^+ and 2-methylpropane under the same pressure conditions. All the ions whose relative abundance was found larger than 10% in at least one case are mentioned. When no' value is indicated the corresponding relative abundance is less than 1%.

Reacting ion	(b) 40	48	51	52 (a)	55 (a)	56	59	58	63	64 (a)	40
Product ions (mass)	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ar
M^+(m)	100	100	39	100	100	100	51	90	86	30	--
$C_3H_5^+$(41)	--	1	--	--	--	6	11	7	4	3	3
$C_3H_7^+$(43)	--	2	1	1	1	16	26	18	15	10	2
$C_4H_9^+$(57)	4	10	32	15	30	66	71	100	34	100	100
$C_3H_6M^+$(m+42)	--	--	--	--	--	74	100	50	--	--	--
$C_4H_8M^+$(m+56)	--	10	5	1	--	62	21	3	7	--	--
$C_4H_{10}M^+$(m+58)	--	--	3	98	16	4	3	2	100	59	--
$C_4H_{11}M^+$(m+59)	2	--	--	5	6	17	4	10	4	3	--
$C_4H_{12}M^+$(m+60)	--	--	--	--	--	35	47	81	--	--	--
$C_5H_{12}M^+$(m+72)	--	23	1	--	--	2	--	--	--	--	--
$C_5H_{13}M^+$(m+73)	--	2	2	--	--	18	--	--	--	--	--
$C_5H_{14}M^+$(m+74)	--	5	5	--	--	34	6	5	--	--	--
$C_5H_{15}M^+$(m+75)	--	--	--	--	--	16	1	--	--	--	--
$C_7H_{12}M^+$(m+96)	--	29	--	--	--	--	--	2	--	--	--
$C_7H_{16}M^+$(m+100)	--	2	--	--	--	70	58	70	--	--	--
$C_8H_{14}M^+$(m+110)	--	92	100	--	--	--	--	--	--	--	--
$C_8H_{15}M^+$(m+111)	--	16	12	--	--	2	5	6	--	--	--
$C_8H_{16}M^+$(m+112)	--	4	54	--	--	--	1	1	--	--	--
$C_8H_{17}M^+$(m+113)	--	4	12	3	--	3	--	--	--	--	--
$C_8H_{18}M^+$(m+114)	--	--	17	--	--	48	14	4	--	--	--
$C_8H_{20}M^+$(m+116)	--	--	--	57	--	3	1	4	67	--	--

(a) $M(H_2O)^+$(m+18) ions are also observed, since H_2O was present as an impurity.

(b) other isotopes studied : ^{46}Ti, ^{53}Cr, ^{54}Fe, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{68}Zn.

reacted with 2-methylpropane under the same conditions. No unreacted Ar^+ could be detected, indicating a much larger cross section than in the preceding cases. Only one reaction is observed : hydride abstraction affording $C_4H_9^+$. At low energy Ar^+ was reported to react with ethane giving $C_2H_5^+$ among other products and no charge transfer reaction (28).

In conclusion, the use of triple quadrupole mass spectrometry coupled with a FAB ion source allowed to compare the gas phase chemistry of different metal ions. This chemistry is extremely specific depending on the nature of the metal, and the possibility of multiple collisions appears to enhance this specificity. Another important feature is the formation of $M(C_4H_{10})^+$ complexes : such an addition of an alkane to a metal ion, which had never been reported to occur directly, probably requires both low collision energy and relatively high pressure. The structures of the different reaction products are under investigation.

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