Electronic Supplementary Material

CF_3^+ and CF_2H^+: new reagents for n-alkane determination in chemical ionisation reaction mass spectrometry

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		[(a)] CF_2H^+	[(a)] CF_3^+	[(b)] CF_3^+
methane	CH_4			
ethane	C_2H_6	5.5	3.7	3.2
propane	C_3H_8	8.6	5.9	5.0
n-butane	C_4H_{10}	11.8	7.5	6.2
n-pentane	C_5H_{12}	13.1	8.9	8.9
n-hexane	C_6H_{14}		10.5	8.6

Table S-1. Rate Coefficients of Hydride Transfer with linear n-alkanes (k /10^{-10} cm^3 $molecule^{-1}$ s^{-1})

a. Source: Lias et al. [18]

b. Source: Dehon et al.[20]

Name	*m/z*	Fragments	% (CF_4)	%(O_2)	% CF_3^+
Ethane C_2H_6	26	$C_2H_2^+$		1	80
	27	$C_2H_3^+$		2	
	28	$C_2H_4^+$		14	
	29	$C_2H_5^+$	99	83	
Propane C_3H_8	26	$C_2H_2^+$		1	77
	27	$C_2H_3^+$		1	
	28	$C_2H_4^+$		28	
	29	$C_2H_5^+$	1	4	
	41	$C_3H_5^+$		2	
	43	$C_3H_7^+$	99	64	
n-Butane C_4H_{10}	26	$C_2H_2^+$		<1	82
	27	$C_2H_3^+$		1	
	28	$C_2H_4^+$		3	
	29	$C_2H_5^+$	1	3	
	41	$C_3H_5^+$		2	
	43	$C_3H_7^+$	1	73	
	57	$C_4H_9^+$	96	17	
n-Pentane C_5H_{12}	28	$C_2H_4^+$		1	60
	29	$C_2H_5^+$		3	
	41	$C_3H_5^+$		5	
	42	$C_3H_6^+$		2	
	43	$C_3H_7^+$	6	45	
	56	$C_4H_8^+$		3	
	57	$C_4H_9^+$	1	11	
	71	$C_5H_{11}^+$	93	30	
n-Hexane C_6H_{14}	29	$C_2H_5^+$		<1	64
	41	$C_3H_5^+$		1	
	43	$C_3H_7^+$	20	5	
	56	$C_4H_8^+$		28	
	57	$C_4H_9^+$	5	42	
	58	$C_4H_{10}^+$		3	
	71	$C_5H_{11}^+$	1	3	
	85	$C_6H_{13}^+$	74	17	

Table S-2. Relative abundance of observed ions at E/N=50Td. The relative abundance of CF_2H^+/*CF_2H^+ + CF_3^+) was higher for standards prepared in Tedlar bags. This resulted in a reduced relative yield of CF_3^+(shown in the rightmost column).

Name	*m/z*	Fragments	% (CF_4)	%(O_2)	% CF_2H^+
Ethane C_2H_6	26	$C_2H_2^+$		2	99.6
	27	$C_2H_3^+$	4	10	
	28	$C_2H_4^+$		30	
	29	$C_2H_5^+$	94	57	
Propane C_3H_8	26	$C_2H_2^+$		2	99.2
	27	$C_2H_3^+$		2	
	28	$C_2H_4^+$		36	
	29	$C_2H_5^+$	1	11	
	41	$C_3H_5^+$	2	4	
	43	$C_3H_7^+$	97	45	
n-Butane C_4H_{10}	26	$C_2H_2^+$		<1	99.6
	27	$C_2H_3^+$		1	
	28	$C_2H_4^+$		3	
	29	$C_2H_5^+$	1	8	
	41	$C_3H_5^+$		7	
	42	$C_3H_6^+$		2	
	43	$C_3H_7^+$	1	74	
	57	$C_4H_9^+$	96	4	
n-Pentane C_5H_{12}	27	$C_2H_3^+$		<1	99.3
	29	$C_2H_5^+$		2	
	41	$C_3H_5^+$		20	
	42	$C_3H_6^+$		8	
	43	$C_3H_7^+$	25	52	
	56	$C_4H_8^+$		4	
	57	$C_4H_9^+$		11	
	58	$C_4H_{10}^+$		<1	
	71	$C_5H_{11}^+$	75	3	
n-Hexane C_6H_{14}	29	$C_2H_5^+$		1	99.3
	41	$C_3H_5^+$	2	7	
	42	$C_3H_6^+$		1	
	43	$C_3H_7^+$	48	8	
	56	$C_4H_8^+$		31	
	57	$C_4H_9^+$	6	47	
	58	$C_4H_{10}^+$		2	
	71	$C_5H_{11}^+$	<1	2	
	85	$C_6H_{13}^+$	44	1	

Table S-3. Relative abundance of observed ions at E/N=100Td. The relative abundance of $CF_2H^+/(CF_2H^+ + CF_3^+)$ was higher for analytes prepared in Tedlar bags. This resulted in a reduced relative yield of CF_3^+(shown in the rightmost column).

		100Td		50Td	
Name	Fragment	S:N	LOD (ppm)	S:N	LOD (ppm)
Ethane	$C_2H_5^+$	2678	0.006	4755	0.003
Propane	$C_3H_7^+$	1046	0.014	1277	0.011
n-Butane	$C_4H_9^+$	24002	0.001	52560	0.001
n-Pentane	$C_5H_{11}^+$	2253	0.030	2678	0.030
n-Hexane	$C_6H_{13}^+$	1267	0.017	2249	0.003

Table S-4. Limits of detection (LOD) for the alkane/CF_3^+ reactions for a run of 10 minutes. Operating at 50Td was degraded by increased background noise. Both the Signal to Noise (S:N) and the Limits of Detection (LOD) are calculated in accordance with the IUPAC recommendations [30].

		100Td		50Td	
Name	Fragment	S:N	LOD (ppm)	S:N	LOD (ppm)
Ethane	$C_2H_5^+$	4475	0.003	8182	0.002
Propane	$C_3H_7^+$	4590	0.003	22145	0.001
n-Butane	$C_4H_9^+$	1172	0.013	18076	0.001
n-Pentane	$C_5H_{11}^+$	2363	0.006	10665	0.029
n-Hexane	$C_6H_{13}^+$	1942	0.008	5161	0.003

Table S-5. Limits of detection (LOD) for the alkane/O_2^+ reactions for a run of 10 minutes. Both the Signal to Noise (S:N) and the Limits of Detection (LOD) are calculated in accordance with the IUPAC recommendations.[30]

1. $CF_3^+ + H_2O \rightarrow CF_2H^+ + HOF$ ΔH=+361.7 kJ mol^{-1}
2. $CF_3^+ + H_2O \rightarrow CF_2OH^+ + HF$ ΔH=-142.8 kJ mol^{-1}
3. $CF_2^+ + H_2O \rightarrow CF_2H^+ + OH$ ΔH=-13.2 kJ mol^{-1}
4. $CF_2^{2+} + H_2O \rightarrow CF_2OH^+ + H^+$ ΔH= -1725.5 kJ mol^{-1}
5. $CF_2^+ + CF_4 \rightarrow CF_3^+ + CF_3$ ΔH = -92.185 kJ/mol^{-1}

<u>Table S-6. Thermochemistry Calculations.</u>

MP2/6-311G** calculations, ZPE was taken in to account. At E/N = 100Td, the centre of mass energy due to the electric field in the drift tube was 9.04 kJ mol^{-1} to which should be added the thermal energy of 4.19 kJ mol^{-1} for a total of 13.32 kJ mol^{-1} . A small presence of CF_2OH^+ at m/z=67 was noted in all the spectra. The value of Δ H obtained for reaction 2 above is in reasonable agreement the value of Δ H = -164.5 kJ mol^{-1} reported by Grandinetti et al.[31]

n-Alkane	Mass (amu)	Percentage yield				Rel. CF_3^+ yield wet/dry %
		RH=0.1%	RH=20%	RH=45%	RH=90%	
Ethane	29	100	-	-	40	82/94
Propane	43	100	76	57	45.4	75/90
n-Butane	57	100	82	66	44.9	80/93
n-Pentane	71	100	82	65	44.9	73/82
	43	100	78	60	41.4	
n-Hexane	85	100	72	52	34.6	73/82
	57	100	77	58	44.4	
	43	100	78	58	41.2	

Table S-7. The effect of ambient moisture ranging from 0.1% to 90% RH on the yield of the principal fragments of the n-alkane reactions with CF_3^+ and CF_2H^+. Inspite of the low relative humidity of the analytes, persistent residual moisture in the system had a significant effect on the results. The resolution of the equipment was not sufficient to distinguish between $C_2H_5^+$ and an unidentified group possibly N_2H^+ or COH^+. The variation in the yield of the ion fragments are very similar. The value of E/N was ca. 100 Td, a region where the reactants' yield was most sensitive to small shifts in the value of E/N.