Effect of Chain Length on the Chemical Ionisation Mass Spectra of Methyl n-Alkanoates

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The H_2 and CH_4 chemical ionisation (C.I.) mass spectra of a series of methyl n-alkanoates up to methyl stearate have been determined to examine the relative importance of interaction of the reagent gas ions with the carboxy-function compared to interaction with the hydrocarbon chain as a function of hydrocarbon chain length. For both the H_2 and CH_4 systems interaction of the reagent ions with the carboxy-function leads initially to formation of the protonated ester, MH^+, which sequentially loses CH_3OH and CO. Interaction of the reagent ions with the hydrocarbon chain results primarily in H^- abstraction, leading to $(M - H)^+$. The major decomposition mode of the latter ion is CH_3OH elimination, a reaction which requires a C_4 alkyl chain for the H_2 C.I. and a C_5 alkyl chain for the CH_4 C.I. system. This suggests a seven-membered cyclic transition state for H^+ transfer from the alkyl chain to the OCH_3 group. The relative importance of interaction with the alkyl chain increases rapidly with increasing alkyl chain length for both H_2 and CH_4 reagent gases.

ESTERS were one of the first classes of compounds whose chemical ionisation (C.I.) mass spectra were examined. Using methane as reagent gas Munson and Field[1] determined the CH_4 C.I. mass spectra of a series of propionate esters up to n-octyl propionate as well as a representative selection of other esters. They found that the spectra could be rationalised by assuming predominant attack at the carboxy-group by the major reactant ions CH_5^+, $C_2H_5^+$, and $C_3H_5^+$. By contrast, the CH_4 C.I. of alkanes proceeds[2] entirely by near-random attack on the hydrocarbon chain resulting in H^- or alkanide ion abstraction leading, initially, to $(M - H)^+$ and lower alkyl ions respectively. In a number of cases it has been shown[3,4] that there is no incorporation of hydrogen from the reactant ions into the product ions in the CH_4 C.I. of alkanes.

This differing behaviour of esters and alkanes suggests that in esters containing long alkyl chains one should see not only reactions characteristic of the carboxy-group but also H^- and/or alkanide ion abstraction reactions characteristic of the hydrocarbon portion of the molecule. The longest chain ester which has been studied is methyl octanoate[1] and in the CH_4 C.I. spectrum, in addition to the MH^+ and $(MH - CH_3OH)^+$ ions characteristic of interaction with the $-CO_2CH_3$ function, a moderate intensity $(M - H)^+$ ion is observed, probably corresponding to H^- abstraction from the alkyl chain. In addition, Munson and Field[1] report observation of an ion at m/e 125 (5% of total ionisation), which probably arises by elimination of CH_3OH from the $(M - H)^+$ ion (Scheme). The reaction path outlined in the Scheme requires, initially, H^- abstraction from the alkyl chain and more importantly, an alkyl chain of a length adequate for a hydrogen on the carbon adjacent to the charged site to approach sufficiently close to the methoxy-group to be transferred and subsequently eliminated. A mechanism similar to that outlined in the Scheme undoubtedly is involved in the loss of methanol from the α-cleavage fragment ions of substituted (both alkyl and heteroatomic groups) fatty acid methyl esters.[5]

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[1] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, 1966, **88**, 4337.

[2] F. H. Field, M. S. B. Munson, and D. A. Becker, *Adv. Chem. Series*, 1966, **58**, 167.

[3] D. F. Hunt and C. N. McEwen, *Org. Mass Spectrometry*, 1973, **7**, 441.

[4] B. H. Solka, A. Y.-K. Lau and A. G. Harrison, *Canad. J. Chem.*, 1974, **52**, 1798.

[5] (*a*) R. Ryhage and E. Stenhagen, *Arkiv Kemi.*, 1960, **15**, 291, 333; (*b*) R. Ryhage and E. Stenhagen, *ibid.*, p. 545; (*c*) M. A. Winnik, *Org. Mass Spectrometry*, 1974, **9**, 920.

To examine the importance of attack on the alkyl chain in the C.I. of esters and, in particular, to elucidate the dependence of the methanol elimination reaction on the hydrocarbon chain length, we have determined the H_2 and CH_4 C.I. mass spectra of a series of methyl esters up to methyl stearate. There has been no previous study of the H_2 C.I. of esters and a comparison with the CH_4 results is of interest.

EXPERIMENTAL

The chemical ionisation mass spectra were determined using a Dupont 21-490 mass spectrometer equipped with a high pressure chemical ionisation source. With this instrument source pressures cannot be measured directly, however a probe consisting of a calibrated thermocouple gauge inserted in place of the solid sample probe indicated source pressures of *ca.* 0.5 mm for both hydrogen and methane reagent gases. Spectra obtained using 70 and 460 eV ionising electrons were found to be identical.

Other operating conditions were a source temperature of *ca.* 200°, a heated inlet system temperature of *ca.* 150—200°, with the repellers being held at cage potential. The lower molecular weight esters were admitted to the source through the heated inlet system while methyl decanoate and higher esters were evaporated directly into the source from capillary tubes with restricted orifices contained in the direct introduction probe.

All esters were commercially available samples which showed no detectable impurities in their electron impact mass spectra.

RESULTS AND DISCUSSION

General Features of C.I. Spectra.—For illustrative purposes the H_2 and CH_4 C.I. mass spectra of methyl butyrate and methyl octanoate are shown in Figure 1 while the spectra obtained for methyl stearate are shown in Figure 2. The CH_4 spectrum obtained for methyl octanoate is in good agreement with that reported by Munson and Field.[1]

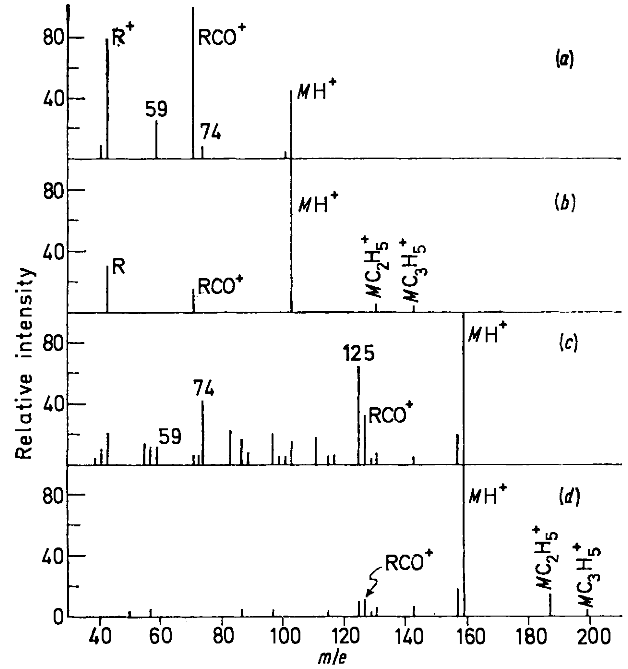


FIGURE 1 (a) H_2 C.I. mass spectrum of $CH_3[CH_2]_2CO_2CH_3$; (b) CH_4 C.I. mass spectrum of $CH_3[CH_2]_2CO_2CH_3$; (c) H_2 C.I. mass spectrum of $CH_3[CH_2]_6CO_2CH_3$; (d) CH_4 C.I. mass spectrum of $CH_3[CH_2]_6CO_2CH_3$

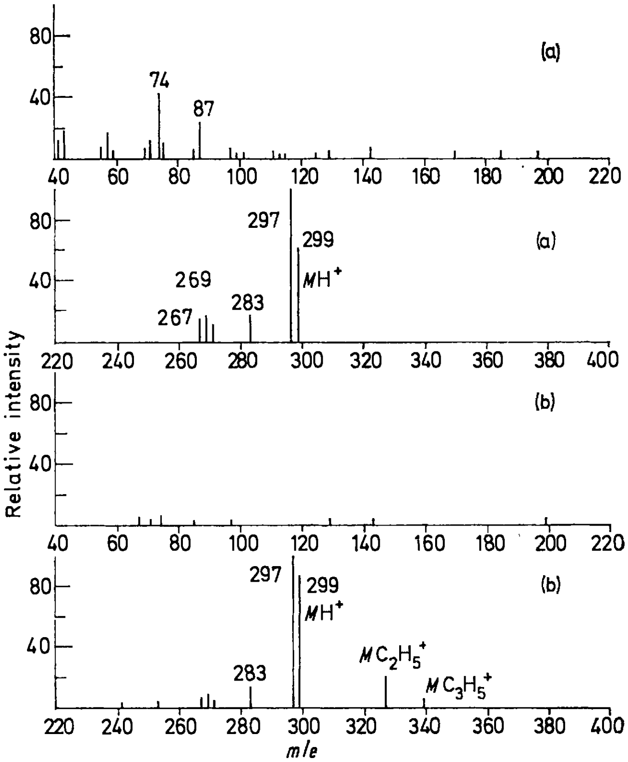


FIGURE 2 (a) H_2 C.I. mass spectrum of methyl stearate; (b) CH_4 C.I. mass spectrum of methyl stearate

The H_2 and CH_4 C.I. spectra of methyl butyrate show the same major fragmentation sequence [reaction (1)], originating from the protonated molecular ion, MH^+.

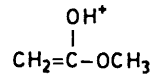
$$RCO_2CH_3{\cdot}H^+ \xrightarrow{-CH_3OH} RCO^+ \xrightarrow{-CO} R^+ \qquad (1)$$

As expected, the RCO^+ and R^+ fragment ions are more intense in the H_2 C.I. spectrum since the initial protonation by H_3^+ is more exothermic * and therefore produces MH^+ ions with greater average excitation.

Two additional fragment ions are observed in the H_2 C.I. spectrum of methyl butyrate at *m/e* 59 and 74, probably corresponding to the ions (*a*) and (*b*) respectively. The *m/e* 59 product was observed in the H_2 C.I.

$^{+}CO_2CH_3$

(*a*)



$$CH_2{=}\overset{\overset{\displaystyle OH^+}{|}}{C}{-}OCH_3$$

(*b*)

spectra of all the methyl esters while *m/e* 74 was observed for methyl butyrate and higher esters. Using D_2 as reagent gas it was shown that neither ion incorporated any hydrogen from the reagent gas. This is not surprising for the ion (*a*) which probably arises either by R$^-$

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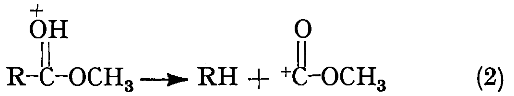
* P.A. (H_2) = 100 kcal mol^{-1} [$\Delta H_f(H_3^+)$ 264 kcal mol^{-1} [6]]. P.A. (CH_4) = 127 kcal mol^{-1},[7] while the proton affinity of methyl esters is *ca.* 200 kcal mol^{-1}.[8]

abstraction from RCO_2CH_3 or by protonation followed by alkane elimination [reaction (2)]. The result is



$$R-\overset{\overset{+}{O}H}{\overset{\|}{C}}-OCH_3 \longrightarrow RH + {}^{+}\overset{\overset{O}{\|}}{C}-OCH_3 \qquad (2)$$

surprising for the *m/e* 74 ion (*b*) and shows that this product does not arise by simple C–C bond cleavage of the carbonyl protonated species but rather must arise either by fragmentation of the $(M - H)^+$ ion or by charge transfer from H_3^+ to the ester. Although ground state H_3^+ has a recombination energy of *ca.* 9.2 eV [$\Delta H_f(H_3^+) = 264$ kcal mol^{-1} [6]] it is distinctly possible that not all the H_3^+ ions in our system are in the ground state; the excited ions will have a considerably higher recombination energy. It is known [9] that H_3^+ is initially formed with considerable excess of energy and requires several collisions to deactivate to the ground state. Although the appearance potential for *m/e* 74 from methyl esters is not known it probably is fairly low since *m/e* 74 comprises the base peak for methyl n-alkanoates larger than hexanoates.[10]

The CH_4 C.I. spectrum of methyl octanoate shows MH^+ as the base peak with significant loss of CH_3OH to form RCO^+ [reaction (1)] although the R^+ ion ($C_7H_{15}^+$, *m/e* 99) is not observed. The $(M - H)^+$ ion is *ca.* 17% of the base peak, while *m/e* 125, corresponding to loss of CH_3OH from $(M - H)^+$, is *ca.* 8% of the base peak. The low intensity *m/e* 97 ion $(C_7H_{13})^+$ may originate by CO loss from the *m/e* 125 ion.

The H_2 C.I. spectrum of methyl octanoate also shows MH^+ as the base peak, with significant RCO^+ (*m/e* 127) and a low intensity R^+ ion (*m/e* 99), the products expected from protonation at the carboxy-group followed by fragmentation. The products resulting from H^- abstraction from the alkyl chain are much more pronounced than in the CH_4 spectrum with $(M - H)^+$ being 19% of the base peak and $[M - (H + CH_3OH)]^+$ (*m/e* 125) being *ca.* 63% of the base peak. Further, the *m/e* 97 ion (20% of base peak) may originate by loss of CO from the *m/e* 125 ion.

In addition to the *m/e* 59 and 74 ions observed in the H_2 C.I. spectrum of methyl butyrate the H_2 C.I. spectrum of methyl octanoate shows a considerable range of ions of low abundance. These appear to consist of the following series of ions, observed for all the higher esters: (i) alkenyl ions (*m/e* 41, 55, 83, 97, . . .); (ii) alkyl ions (*m/e* 43, 57, 71, 85, . . .); (iii) a series resulting nominally from alkanide ion abstraction (*m/e* 73, 87, 101, 115, 129, 143, . . .); and (iv) a series resulting nominally from olefin elimination from MH^+ (*m/e* 131, 117, 103, 89). This plethora of ions at masses below the molecular weight of the ester obviously would create difficulties in attempts to analyse mixtures of methyl alkanoates by H_2 C.I. mass spectrometry; the CH_4 C.I. spectra are much simpler.

In the CH_4 C.I. spectrum of methyl stearate the $(M - H)^+$ ion is the base peak with MH^+ being *ca.* 87%. Obviously with the C_{17} alkyl chain the probability of attack on the alkyl chain has become as important as attack at the carbonyl group. The former leads almost exclusively to H^- abstraction although the low abundance ions at *m/e* 283, 269, and 241 may represent alkanide ion abstraction reactions. Apart from the $MC_2H_5^+$ and $MC_3H_5^+$ cluster ions, the only other ions of significant intensity are *m/e* 271 $(MH - C_2H_4)^+$ and 267 $(MH - CH_3OH)^+$.

In the H_2 C.I. spectrum of methyl stearate the $(M - H)^+$ ion is again the base peak with MH^+ being *ca.* 60% of the base peak. Again low intensity ions resulting nominally from alkanide ion abstraction are observed at *m/e* 283, 269, and below 200. The ubiquitous *m/e* 59 and 74 ions are observed as well as a number of low mass alkyl and alkenyl ions. In the high mass region the only other ions of significance are *m/e* 271 and 267, as observed in the CH_4 C.I. spectrum.

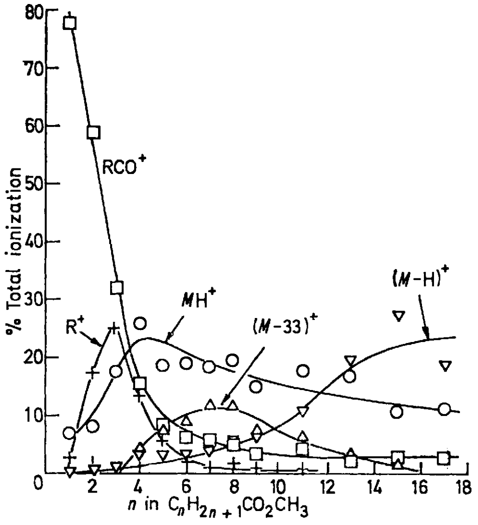


FIGURE 3 Dependence of ion abundances on chain length, H_2 C.I.

Dependence of H^- *Abstraction and Subsequent* CH_3OH *Loss on Chain Length.*—In Figure 3 we show graphically the dependence on alkyl chain length of the mechanistically important ions in the H_2 C.I. of methyl n-alkanoates. The intensities are expressed as % of total ionisation, disregarding the reagent gas ions in deriving the total ionisation. The two major reaction sequences of interest are reaction (1), protonation followed by successive loss of CH_3OH and CO and the sequence outlined in the Scheme, H^- abstraction followed by loss of CH_3OH. These two sequences are characteristic of interaction

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[6] M. E. Schwartz and L. J. Schaad, *J. Chem. Phys.*, 1967, **47**, 5325.

[7] W. A. Chupka and J. A. Berkowitz, *J. Chem. Phys.*, 1971, **54**, 4256.

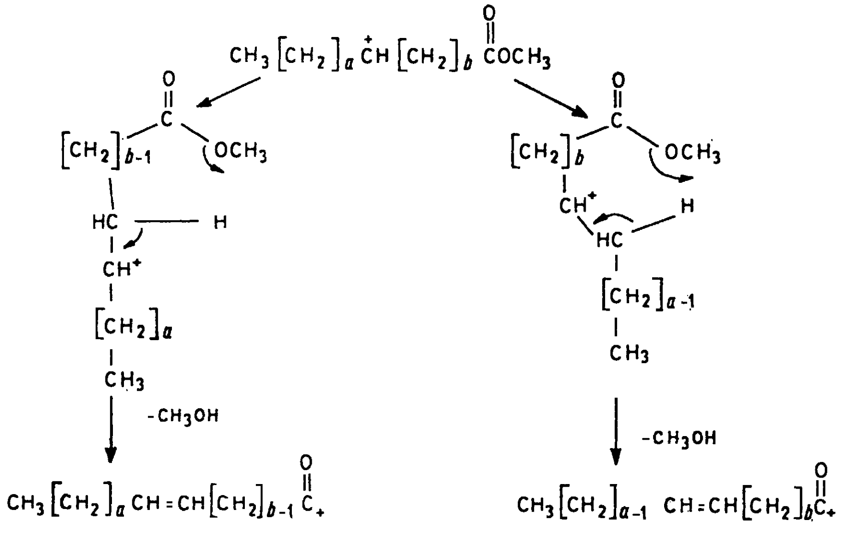
[8] J. Long and B. Munson, *J. Amer. Chem. Soc.*, 1973, **95**, 2427.

[9] (*a*) J. J. Leventhal and L. Friedman, *J. Chem. Phys.*, 1968, **49**, 1974; (*b*) M. T. Bowers and D. D. Elleman, *J. Amer. Chem. Soc.*, 1970, **92**, 7258.

[10] H. Budzikiewica, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1970.

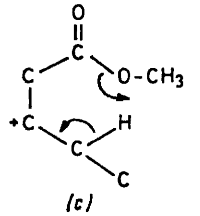
with the carboxy-function and with the hydrocarbon chain, respectively.

For methyl acetate, methyl propionate, and methyl n-butyrate >70% of the total ionisation resides with $RCO_2CH_3H^+$, RCO^+, and R^+ characteristic of protonation at the carboxy-group followed by fragmentation, with the extent of fragmentation decreasing rapidly with increasing molecular size. With increasing alkyl chain length the importance of this reaction channel decreases, accounting for only *ca.* 14% of the total ionisation in methyl stearate. Other fragmentation modes of the protonated ester, such as olefin elimination, have not been considered in deriving this total.

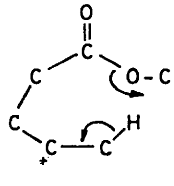


SCHEME

Formation of $(M-H)^+$ presumably by H^- abstraction, is observed in low intensity even for methyl acetate but increases significantly in importance for esters larger than methyl butyrate and becomes the base peak for n-$C_{13}H_{27}CO_2CH_3$ and higher esters. The peak $(M-33)^+$, corresponding to loss of CH_3OH from the $(M-H)^+$ ion, is not observed for methyl butyrate and shorter esters, but is significant (4.2%) for methyl n-pentanoate. The abundance of this fragment ion initially increases rapidly but decreases beyond methyl n-nonanoate as the excess energy in the $(M-H)^+$ ion is more effectively randomised, leaving insufficient energy for fragmentation. The sharp onset for the formation of $(M-33)^+$ at methyl n-pentanoate implies for the H^+ transfer step in the Scheme a six-membered transition state (*c*) if the terminal primary hydrogen cannot be transferred or, alternatively, a seven-membered transition state (*d*) if the terminal methyl hydrogen can be transferred.



(*c*)



(*d*)

It is possible that the seven-membered ring is necessary to achieve a closer approach to planarity. There is evidence[11] for a strong preference for a linear geometry in the formation of intramolecular hydrogen bonds in gas-phase protonated molecules.

Figure 4 shows a similar plot of ion intensities (% of total ionisation, excluding reagent gas ions) as a function of chain length for the major ions in the CH_4 C.I. mass spectra of methyl n-alkanoates. The spectra of the esters lower than methyl butyrate were not obtained because of the overlap of product ions with reagent gas ions.

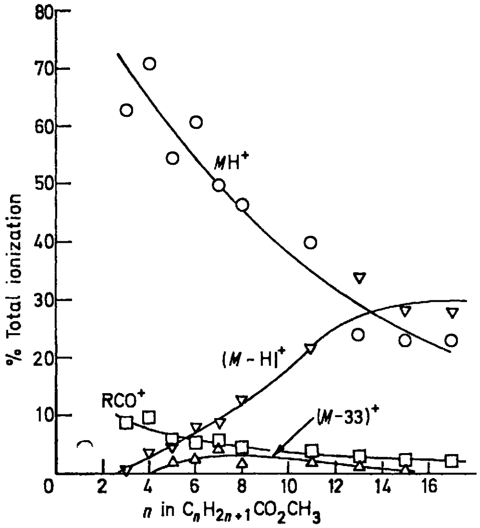


FIGURE 4 Dependence of ion abundances on chain length, CH_4 C.I.

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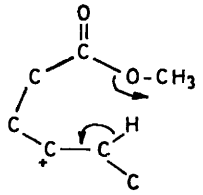
[11] (*a*) J. L. Beauchamp, *Ann. Rev. Phys. Chem.*, 1971, **22**, 527; (*b*) T. H. Morton and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 1972, **94**, 3671; (*c*) D. H. Aue, H. M. Webb and M. T. Bowers, *J. Amer. Chem. Soc.*, 1973, **95**, 2699.

Protonation by CH_5^+ or $C_2H_5^+$, the major reactant ions in methane, is much less exothermic than protonation by H_3^+, with the result that the abundance of MH$^+$ is considerably greater and those for RCO$^+$ or R$^+$ are considerably lower than in the corresponding H_2 C.I. spectrum. As for the hydrogen results, the MH$^+$ and RCO$^+$ ions characteristic of interaction of the reagent ions with the carboxy group, predominate for the lower esters but decrease in relative importance as the alkyl chain becomes longer. With increasing chain length the $(M - H)^+$ and $(M - 33)^+$ ions, characteristic of interaction with the hydrocarbon chain, become of increasing importance; indeed for the highest esters studied, n-$C_{15}H_{31}CO_2CH_3$ and n-$C_{17}H_{35}CO_2CH_3$ the $(M - H)^+$ ion is the base peak in the spectrum. Hydride ion abstraction by CH_5^+ or $C_2H_5^+$ is less exothermic than hydride ion abstraction by H_3^+ and, as expected, the loss of CH_3OH from the $(M - H)^+$ ion is less important. Loss of CH_3OH from the $(M - H)^+$ ion is observed only for methyl n-hexanoate and longer chain esters. The minimum chain length is one carbon greater than for the H_3^+ system. In the CH_4 case, since the $(M - H)^+$ ion has less internal excitation energy, the elimination of CH_3OH may be more critically dependent on the activation energy for the reaction. Formation of a terminal double bond requires *ca.* 2 kcal mol^{-1} greater energy than formation of a non-terminal double bond. The results for the CH_4 system are consistent with the results for the H_2 system if we assume for the former that H$^+$ transfer in the Scheme cannot occur from the terminal methyl group but does require a seven-membered transition state (*e*).



(e)

Obviously deuterium labelling is required to determine the origin of the H$^+$ transferred in both the H_2 and CH_4 C.I. systems. For longer hydrocarbon chain lengths transition states larger than seven-membered are possible and, indeed, probably are also involved. The initial increase in the $[(M - (H + CH_3OH)]^+$: $(M - H)^+$ ratio with chain length in both the H_2 and the CH_4 C.I. systems can be rationalised in terms of the increase, with chain length, of the fraction of conformations of a flexible hydrocarbon chain which place a hydrogen in a position appropriate for transfer to the methoxy-group.[12]

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[5/568 *Received, 24th March,* 1975]

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[12] M. A. Winnik, C. K. Lee, and P. T. Kwong, *J. Amer. Chem. Soc.*, 1974, **96**, 2901.