An Electron-Impact Study of Ionization and Dissociation in Methoxy- and Halogen-Substituted Methanes[1]

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Abstract: Appearance potentials and standard heats of formation of a number of methoxy- and halogen-substituted methyl ions have been determined. Combination of the data with known free-radical ionization potentials results in $\Delta H_f(CH_3O\cdot) = +5 \pm 2$ kcal/mole, $\Delta H_f(CH_3OCH_2\cdot) = -12 \pm 3$ kcal/mole, and $D[CH_3OCH_2-H] = 82 \pm 3$ kcal/mole. A similar evaluation of the available data for the fluoro-substituted methyl ion gives $\Delta H_f(FCH_2\cdot) = -19 \pm 3$ kcal/mole and $D[FCH_2-H] = 89 \pm 3$ kcal/mole. Stabilization effects in the polymethoxymethyl series display marked saturation. In the polyfluoromethyl series stabilization of CF_3^+ is apparently less than that for HCF_2^+. The recently determined upper limit of 9.5 ev for the ionization potential of the CF_3 radical is reconciled with a number of appearance potentials of this ion and the CF_3-H bond dissociation energy determined from kinetic data. The results obtained for the other halogen compounds appear subject to larger uncertainties.

As part of a program concerned with substituent stabilizing effects on gas phase ions,[2] we have determined the appearance potentials of a number of substituted methyl ions arising from the dissociative ionization of some methoxy- and halogen-substituted methanes. As no comparable studies have been reported for the methoxy-substituted methanes and as the electron-impact results for the halomethanes are in many cases meager or conflicting,[3-11] we report herewith our results.

The results of this investigation provide new information on the stabilizing effects of multiple substitution in the methyl ion and on the relationship between substituent effects in corresponding ion and radical.

Experimental Section

All appearance potential measurements were carried out in a Bendix Model 14-101 time-of-flight mass spectrometer which had been modified by the incorporation of differential pumping on the source region and by an electron gun modification permitting the use of the retarding-potential-difference technique.[12] The potential configurations of the electron gun and source region and the details of the measurements were identical with those reported previously.[13] The energy spread of the pseudo-monoenergetic electron beam was approximately 0.1 ev, and either xenon, krypton, nitric oxide, or carbon monoxide (depending upon the appearance potential and mass of the ion being examined) were used to calibrate the electron energy scale.

Methylal, trimethyl orthoacetate, methyl acetal, and methyl ketal were Eastman Organic Chemicals; trimethyl orthoformate was obtained from Kay-Fries Chemicals, Inc.; methylene chloride, chloroform, and methyl iodide were Fischer Certified Reagents; and a sample of tetramethyl orthocarbonate was kindly donated by Dr. Brian G. Ramsey. All the above compounds were fractionated on a Nester and Foust 27-in. spinning-band column and collected over type 4A molecular sieve. The compounds were degassed at least three times at about 10^{-6} torr prior to introduction into the mass spectrometer.

Dimethyl ether, methyl chloride, carbon monoxide, nitric oxide, xenon, and krypton were obtained from the Matheson Co., Inc.; methyl bromide was obtained from Dow Chemical Co.; fluoroform was obtained from Peninsular Chemical Research, Inc.; and difluoromethane was a gift from Dr. Alfred C. Haven of E. I. du Pont de Nemours and Co., Inc. All gases were subjected to the same degassing procedure but otherwise were used as received.

Methyl ethyl ether was synthesized by the method of Williamson.[14] After fractionation (bp 8-11°) and degassing, mass spectral analysis indicated a purity greater than 98%. Methyl nitrite was prepared by the method of Slater[15] and fractionated over two ice-water traps into a Dry Ice-acetone trap. After a subsequent fractionation at $-127°$ it was degassed. Mass spectral analysis indicated a purity in excess of 95%.

Methyl fluoride was obtained from Columbia Organic Chemical Co., Inc. Mass spectral analysis indicated the presence of some high molecular weight impurities which were removed by gas chromatographic separation on a high activity silica gel column. The mass spectrum of the resulting methyl fluoride was identical with that reported in the "API Tables of Mass Spectra."

Results

Methoxy-Substituted Methanes. The appearance potentials determined for the series of substituted methoxymethanes and the standard heats of formation of the ionic species are shown in Table I. In the calculation of the ionic heats of formation it is assumed that no excess energy is involved in the simple dissociation

$$R_1R_2 + e \longrightarrow R_1^+ + R_2 + 2e \qquad (1)$$

so that the energetic relationship between appearance potential and thermochemical heats of formation may be written as the equality

$$A(R_1^+) = \Delta H_f(R_1^+) + \Delta H_f(R_2) - \Delta H_f(R_1R_2) \qquad (2)$$

In using eq 2 to calculate $\Delta H_f(R_1^+)$, which is in reality

(1) Based upon a thesis submitted by R. H. M. to the Department of Chemistry of The Pennsylvania State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1965.

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Table I. Electron-Impact Energetics in Methoxy-Substituted Methanes

Ion	Molecule	Neutral assumed	AP,[a] ev	ΔH_f(ion), kcal mole^{-1}
NO$^+$	CH$_3$ONO	CH$_3$O	11.07 ± 0.06	5[b]
CH$_3$OCH$_2^+$	CH$_3$OCH$_3$	H	11.42 ± 0.01	167
	CH$_3$OCH$_2$CH$_3$	CH$_3$	11.25 ± 0.07	173
	(CH$_3$O)$_2$CH$_2$	CH$_3$O	11.41 ± 0.03	172
(CH$_3$O)$_2$CH$^+$	(CH$_3$O)$_2$CH$_2$	H	10.38 ± 0.03	101
	(CH$_3$O)$_2$CHCH$_3$	CH$_3$	10.34 ± 0.07	113
	(CH$_3$O)$_3$CH	CH$_3$O	10.36 ± 0.06	112
(CH$_3$O)$_3$C$^+$	(CH$_3$O)$_3$CH	H	10.39 ± 0.05	66
	(CH$_3$O)$_3$CCH$_3$	CH$_3$	10.39 ± 0.10	74
	(CH$_3$O)$_4$C	CH$_3$O	10.32 ± 0.10	68
CH$_3$OC$^+$HCH$_3$	(CH$_3$O)$_2$)$_2$CHCH$_3$	CH$_3$O	10.63 ± 0.04	146
(CH$_3$O)$_2$C$^+$CH$_3$	(CH$_3$O)$_3$CCH$_3$	CH$_3$O	10.37 ± 0.02	131
CH$_3$OC$^+$(CH$_3$)$_2$	(CH$_3$O)$_2$C(CH$_3$)$_2$	CH$_3$O	10.28 ± 0.05	99

[a] The indicated uncertainties represent average deviations from the mean of replicate measurements. [b] ΔH_f(CH$_3$O).

an upper limit, it is obviously necessary to know the heat of formation of the neutral fragment, formed in the dissociation (1), as well as the heat of formation of the parent molecule. As far as the radical heats of formation are concerned, the values ΔH_f(H) = 52.1 kcal/mole[16] and ΔH_f(CH$_3$)[17,18] = 33 ± 1 kcal/mole are well established. There is more uncertainty concerning ΔH_f(CH$_3$O). Gray[19] has examined the available data on the kinetics of decomposition of methyl nitrite and methyl nitrate and using the method of Szwarc[20] has concluded that ΔH_f(CH$_3$)O = −0.5 ± 3 kcal/mole. D'Or and Collin[21] have measured the appearance potential of NO$^+$ from methyl nitrite to be 10.7 ev, which upon taking the ionization potential of NO as 9.25 ev[22,23] leads to the value of −3 kcal/mole. We have re-measured A(NO$^+$) from methyl nitrite as shown in Table I, and our value leads to ΔH_f(CH$_3$O) = +5 kcal/mole. It is likely that within the combined experimental errors all values are in agreement. However, in the calculations of the ionic heats of formation in Table I, we have used our value of ΔH_f(CH$_3$O) = 5 kcal/mole and we note that a substantially lower value of ΔH_f(CH$_3$O) (say ΔH_f(CH$_3$O) < 0) would not give as good an agreement for the heats of formation of ions derived from different sources. Hence, we believe that ΔH_f(CH$_3$O) > 0, and that within the combined experimental errors our value of +5 kcal/mole and Gray's estimate of −0.5 kcal/mole are in agreement. That the formation of NO$^+$ from CH$_3$ONO involves little or no excess energy is indicated by the observations that (1) the ionization efficiency curve of NO$^+$ is simple, that is, there is no long tail characteristic of an excess energy process; and (2) NO$^+$ is the major ion in the mass spectrum, while CH$_3$O$^+$ is only a very minor constituent.

The molecular heats of formation (in kcal/mole) used in constructing Table I are as follows: ΔH_f(NO) = 21.6,[24] ΔH_f(CH$_3$ONO) = −14.9,[24] ΔH_f(CH$_3$OCH$_3$)

= −44.3,[24] ΔH_f(CH$_3$OC$_2$H$_5$) = −53.2,[24] ΔH_f-[(CH$_3$O)$_2$CH$_2$] = −86.1,[25] ΔH_f[(CH$_3$O)$_2$CHCH$_3$] = −93.1,[26] ΔH_f[(CH$_3$O)$_3$CH] = −121.3,[26] ΔH_f-[(CH$_3$O)$_3$CCH$_3$] = −133.0,[27] ΔH_f[(CH$_3$O)$_2$C(CH$_3$)$_2$] = −102.3,[27] and ΔH_f[(CH$_3$O)$_4$C] = −164.5.[27]

m/e **45. CH$_3$OCH$_2^+$.** There is no doubt of the identity of this ion from CH$_3$OCH$_3$ and little doubt when it arises from (CH$_3$O)$_2$CH$_2$. There is a possible ambiguity, however, in the case of m/e 45 from CH$_3$OCH$_2$CH$_3$ since there is the possibility of forming CH$_3$CH$_2$O$^+$. We can rule out this possibility, however, since ΔH_f(C$_2$H$_5$O$^+$) is known. The measurements of Kanomata[28] on (C$_2$H$_5$)$_2$O give ΔH_f(C$_2$H$_5$O$^+$) = 253 kcal/mole. Combining this heat of formation with the appropriate thermochemical data[24] gives a value of 11.3 ev for the ionization potential of the CH$_3$CH$_2$O· radical. We may thus conclude (1) if CH$_3$CH$_2$O$^+$ were formed in a simple dissociation process involving no excess energy (which is unlikely by Stevenson's rule,[29] since I(CH$_3$CH$_2$O) = 11.3 ev as compared with I(CH$_3$OCH$_2$) = 7.95 ev[30]), its appearance potential would be 14.7 ev, not 11.25 as measured. (2) Again invoking Stevenson's rule,[29] the ionization potentials of the alkoxy radicals are sufficiently high to preclude the formation of alkoxy ions in simple dissociation processes when competing dissociations forming alkoxymethyl ions ROCH$_2^+$, (RO)$_2$CH$^+$, etc., are available. (3) The agreement of ΔH_f(CH$_3$OCH$_2^+$) calculated from the appearance potentials confirms the common structure of the ion.

We therefore conclude ΔH_f(CH$_3$OCH$_2^+$) = 170 ± 3 kcal/mole. Moreover, if we combine the value I(CH$_3$OCH$_2$) = 7.95[30] with our result for ΔH_f(CH$_3$-OCH$_2^+$), we arrive at the free-radical heat of formation, ΔH_f(CH$_3$OCH$_2$) = −14 ± 3 kcal/mole. This figure leads to the dissociation energy D[CH$_3$OCH$_2$–H] = 82 ± 3 kcal/mole.

m/e **75. (CH$_3$O)$_2$CH$^+$.** Applying the same criteria as above (namely the unlikelihood of forming alkoxy

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ions in simple dissociative ionization processes when others are available) suggests strongly that m/e 75 has the structure shown in the case of formation from the molecules $(CH_3O)_2CHCH_3$ and $(CH_3O)_3CH$. This conjecture receives further support in the agreement of the ΔH_f values calculated in these two cases. On the other hand, in the case of m/e 75 from $(CH_3O)_2CH_2$, it seems at first sight that the ion could be CH_3-$OCH_2OCH_2^+$ as well as $(CH_3O)_2CH^+$. The latter is in our opinion to be favored, however, since it is clear from the trends in Table I that the appearance potential (AP) for $(CH_3O)_2CH^+$ should be substantially less than that for $CH_3OCH_2^+$ (from any of the neutrals), whereas the AP for $CH_3OCH_2OCH_2^+$ from $(CH_3O)_2CH_2$ would not be expected to differ much from that of $CH_3OCH_2^+$ from CH_3OCH_3. Although the value of ΔH_f calculated for the ion of m/e 75 (Table I) from its appearance potential from $(CH_3O)_2CH_2$ is not in precise agreement with that calculated from the other two compounds, it is likely the same ion and the figures are not outside of the combined errors. We hence assign the value $\Delta H_f[(CH_3O)_2CH^+] = 109 \pm 3$ kcal/mole.

m/e **105.** $(CH_3O)_3C^+$. There is little doubt that this ion has the tertiary structure shown above when it is formed from $(CH_3O)_3CCH_3$ and $(CH_3O)_4C$. In the case of formation from $(CH_3O)_3CH$, we do not know that it is not $(CH_3O)_2CHOCH_2^+$. The arguments by analogy used previously would again tend more toward favoring the tertiary ion structure $(D[(CH_3)_3C-H]$ is 5 kcal/mole less than $D[(CH_3)_2CH-H]^{24}$ and $I[(CH_3)_3C]^{31}$ is 0.48 ev less than $I[(CH_3)_2CH]^{32}$). The argument is supported by the fact that the three calculated values of $\Delta H_f[(CH_3O)_3C^+]$ of Table I are equal within experimental error. We conclude that $\Delta H_f[(CH_3O)_3C^+] = 69 \pm 3$ kcal/mole.

The other ions shown in Table I all involve loss of a CH_3O group and hence there is no ambiguity of their identities.

Halogen-Substituted Methanes. The results of our appearance potential studies on halogen-substituted methanes are shown in Table II. Since the dissocia-

species, the following thermochemical data in kcal/mole were used: $\Delta H_f(CH_3F) = -56.0,^{33}$ $\Delta H_f(CH_2F_2) = -107.2,^{33}$ $\Delta H_f(CHF_3) = -165.1,^{33}$ $\Delta H_f(CH_3Cl) = -20.6,^{33}$ $\Delta H_f(CH_2Cl_2) = -22.4,^{33}$ $\Delta H_f(CHCl_3) = -25.0,^{33}$ $\Delta H_f(CH_3Br) = -10,^{34}$ and $\Delta H_f(CH_3I) = -5.^{34}$

CF_3^+. The formation of CF_3^+ from fluorine derivatives of methane has been studied by many workers, and the over-all result has been a set of low values (96–101 kcal/mole) and a set of high values (118–121 kcal/mole) for $\Delta H_f(CF_3^+)$. Our value of 106 kcal/mole tends to support the lower set. Previously, the high value for $\Delta H_f(CF_3^+)$, namely 120 kcal/mole, was to be preferred since, when it was combined with the directly measured $I(CF_3) = 10.1$ ev,[4] it gave $\Delta H_f(CF_3) = -114$; this value is in good agreement with the value of -115 ± 2 determined from kinetic data.[35] However, very recently Fisher, Homer, and Lossing,[36] from a study of the ionization potentials of larger perfluoroalkyl radicals, have concluded that the previous directly measured value[5] includes >0.6 ev of excitation energy so that the true value should be <9.5 ev. This finding justifies the use of $I_z(CF_3) = 9.3$ ev which was suggested from earlier electron-impact experiments.[37,38] Adopting this lower value for $I_z(CF_3)$ leads to $\Delta H_f(CF_3) = -114 \pm 4$ kcal/mole if the average value of the low group, namely, $\Delta H_f(CF_3^+) = 101 \pm 3$, is used. On the other hand, the use of the average of the high group, namely, $\Delta H_f(CF_3^+) = 120 \pm 2$, leads to the improbably high value of -95 ± 3 for $\Delta H_f(CF_3)$. Thus we conclude from all the data that $\Delta H_f(CF_3^+) = 101 \pm 3$ kcal/mole.

CHF_2^+. Comparatively little work has been reported on the energetics of formation of this ion. Hobrock and Kiser[11] find from its appearance potential from CHF_2Cl that $\Delta H_f(CHF_2^+) = 150$ kcal/mole, which is in reasonable agreement with our value from CF_2H_2 of 144 kcal/mole. On the other hand, Hobrock and Kiser[11] find $\Delta H_f(CHF_2^+) = 197$ kcal/mole from the appearance potential of the ion in CF_3H. This latter value is surely too high. We thus conclude that the "best" value of $\Delta H_f(CHF_2^+) = 147 \pm 3$ kcal/mole. When this is combined with the directly measured ionization potential of CHF_2, viz., $I_f(CHF_2) = 9.45$ ev,[39] a value of $\Delta H_f(CHF_2) = -71 \pm 3$ kcal/mole is obtained.

CH_2F^+. To our knowledge no work has been reported on appearance potential studies of this ion. Combining $I_z(CH_2F) = 9.37$ ev[39] with our appearance potential leads to $\Delta H_f(CH_2F) = -19 \pm 3$ kcal/mole.

CCl_3^+. Many studies of the appearance potentials of CCl_3^+ from $CCl_4,^{4,5,7a,5}$ $CCl_3Br,^5$ and CCl_3F^9 have led to values of $\Delta H_f(CCl_3^+)$ that are in good agreement

Table II. Electron-Impact Energetics in Halogen-Substituted Methanes

Ion	Molecule	Rel intensity of 50 ev	AP, ev[a]	ΔH_f(ion), kcal/mole
CH_2F^+	CH_3F	89.5	13.25 ± 0.06	197
CHF_2^+	CH_2F_2	95.6	13.14 ± 0.02	144
CF_3^+	CHF_3	100.0	14.03 ± 0.06	106
CH_2Cl^+	CH_3Cl	11.4	12.98 ± 0.07	226
$CHCl_2^+$	CH_2Cl_2	2.0	12.12 ± 0.05 (?)	205
CCl_3^+	$CHCl_3$	1.3	11.70 ± 0.09 (?)	193
CH_2Br^+	CH_3Br	11.1	12.12 ± 0.09 (?)	217
CH_2I^+	CH_3I	14.1	12.08 ± 0.09	221

[a] The indicated uncertainties represent average deviations from the mean of replicate determinations.

tion process involves the loss of a hydrogen atom in all cases, there is no uncertainty in the identity of the ions. In calculating the heats of formation of the ionic

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and which average to $\Delta H_f(CCl_3^+)$ = 215 ± 4 kcal/mole. Our value of ΔH_f = 194 kcal/mole is much too low and is undoubtedly due to uncertainties arising from the very low abundance of this ion (1.3 %) in the mass spectrum of chloroform. The low value was probably obtained because of a significant contribution from the ion $CHCl_3^+$ which appears at 11.42 ev.[40] Excluding our value from the other determinations and combining $\Delta H_f(CCl_3^+)$ with the directly measured $I_z(CCl_3)$ = 8.78 ev, we arrive at $\Delta H_f(CCl_3)$ = 13 ± 4 kcal/mole.

$CHCl_2^+$. Our value of 12.12 ev for the appearance potential of this ion from CH_2Cl_2 is considerably lower than the value of 13.00 ev found by Gutbier[6] and Reed and Snedden.[7b] Our value leads to $\Delta H_f(CHCl_2^+)$ = 205, while the higher appearance potential yields $\Delta H_f(CHCl_2^+)$ = 227 kcal/mole. Both values, however, are very uncertain because of the low intensity of the ion in the mass spectrum ($\sim$2%). More meaningful heats of formation have been obtained in studies of $CHCl_2^+$ formed from $CHCl_3$[10,11] and $CHCl_2Br$.[10] The results of these workers yield a "best" value $\Delta H_f(CHCl_2^+)$ = 215 ± 1 kcal/mole, which combined with $I(CHCl_2)$ = 9.30 ev leads to $\Delta H_f(CHCl_2)$ = 1 ± 2 kcal/mole.

CH_2Cl^+. Our appearance potential of 12.98 ev for the formation of this ion from CH_3Cl agrees within experimental error with the value of 12.88 found by Harrison and Shannon.[10] These lead to ionic heats of formation of 226 and 224 kcal/mole, respectively, and differ from the value of 235 kcal/mole found by Gutbier[6] by an amount somewhat outside the combined experimental error. Measurements of the appearance potential of the ion from CH_2Cl_2 have been reported by Gutbier,[6] Harrison and Shannon,[10] and Reed and Snedden[7b] which yield, respectively, $\Delta H_f(CH_2Cl^+)$ values of 235, 231, and 247. The last value is in serious disagreement with the other values reported although the reason is not clear. At any event it has been discarded in attempting to arrive at a "best" value for $\Delta H_f(CH_2Cl^+)$. Harrison and Shannon[10] have also measured the appearance potential of CH_2Cl^+ from CH_2ClBr and find from their result that $\Delta H_f(CH_2Cl^+)$ = 229 kcal/mole. A measurement of the appearance potential of the ion from CH_3CH_2Cl[10] yields 248 kcal/mole for $\Delta H_f(CH_2Cl^+)$. This high value is expected according to Stevenson's rule,[29] since C_2H_5 has a lower ionization potential by $\sim$0.6 ev than CH_2Cl, and, accordingly, the process involving CH_3Cl^+ formation should involve excess energy. From the results discussed we suggest a "best" value of $\Delta H_f(CH_2Cl^+)$ = 230 ± 4 kcal/mole. Combination with $I(CH_2Cl)$ = 9.34 ev[39] yields $\Delta H_f(CH_2Cl)$ = 16 ± 4 kcal/mole.

CH_2Br^+. Our appearance potential from CH_3Br gives $\Delta H_f(CH_2Br^+)$ = 217 kcal/mole, which is unexpectedly low. This value is rejected in favor of Reed and Snedden's[7b] value of 225 determined from CH_2Br_2, and Gutbier's[6] values of 237 from CH_3Br and 238 from CH_2Br_2. The "best" value of $\Delta H_f(CH_2Br^+)$ = 233 ± 6 kcal/mole. $\Delta H_f(CH_2Br)$ is determined by combination with $I(CH_2Br)$ = 9.30[39] to be 18 ± 5 kcal/mole. This value is equivalent to $D(CH_2Br-H)$ = 83 ± 5 kcal/mole, which appears to be satisfactorily in line with the values for $D(CH_2F)$ and $D(CH_2Cl)$ shown in

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Table III. It also appears to accord with a comparison of the magnitude of the activation energies for H-atom abstraction by methyl radicals.[41]

**Table III.** Thermochemical Data on Halogen-Substituted Methanes from Electron-Impact Measurement

Radical R·	$\Delta H_f(R^+)$, kcal/mole	$\Delta H_f(R\cdot)$, kcal/mole	$D[R-H]$, kcal/mole
CH_2F	197 ± 2	−19 ± 3	89 ± 3
CH_2Cl	230 ± 4	16 ± 5	88 ± 5
CH_2Br	233 ± 6	18 ± 5	83 ± 5
CH_2I	221 ± 2	...	...
CHF_2	147 ± 3	−71 ± 5	88 ± 5
$CHCl_2$	215 ± 1	1 ± 2	75 ± 2 (?)
CF_3	101 ± 3	−114 ± 4	103 ± 4
CCl_3	215 ± 4	13 ± 4	90 ± 4

CH_2I^+. There are to our knowledge no other reported measurements for this ion, nor is their available a radical ionization potential to permit calculation of $\Delta H_f(CH_2I)$.

In Table III we summarize the above discussion and present what we believe are the "best" values currently available from electron impact techniques for ionic heats of formation, radical heats of formation, and C–H dissociation energies in halogen-substituted methanes. The dissociation energies of C–H bonds in the halogen-substituted methanes are generally in accord with the magnitude suggested by bond energy calculations[42] and activation energies for H-atom abstraction by methyl radicals.[41] The exception is $D[CHCl_2-H]$ which appears to be much too low. Either $\Delta H_f(CHCl_2^+)$ is too low, which seems unlikely although there have been higher values reported,[6,7b] or the vertical ionization potential determination of $CHCl_2$[39] may involve excess energy. We cannot at this time resolve the difficulty.

Discussion

It is useful to consider the results of Tables I and III from the standpoint of the stabilization effects of substituents in the methyl ion and radical. For radicals this may be done by reference to the hydrogen atom transfer reaction

$$CH_3X(g) + \cdot CH_3(g) = \cdot CH_2X(g) + CH_4(g) \qquad (3)$$
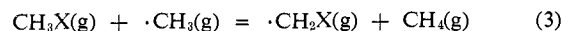
The stabilization energy (SE) of the substituted methyl radical (relative to $\cdot CH_3$) is obtained as follows

$$SE \equiv -\Delta E(_3) = D[CH_3-H] - D[XCH_2-H]$$

For ions the reference reaction is the hydride ion transfer[2]

$$CH_3X(g) + {}^+CH_3(g) = {}^+CH_2X(g) + CH_4(g) \qquad (4)$$

$$SE \equiv -\Delta E(_4) = A[CH_3^+] - A[{}^+CH_2X]$$

Table IV illustrates the rapid saturation of stabilization which is observed in the methyl ion by successive substitution of the methoxy group. Successive substitution of the fluoro substituent apparently leads to no further stabilization. In fact, CF_3^+ appears to be destabilized relative to FCH_2^+ or F_2CH^+.

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Table IV. Stabilization Energy (Relative to CH_3^+) of Polysubstituted Methoxy- and Fluoromethyl Cations

Ion	SE ± 3 kcal/mole
$CH_3OCH_2^+$	66
$(CH_3O)_2C^+H$	85
$(CH_3O)_3C^+$	90
FCH_2^+	27
F_2CH^+	26
F_3C^+	14

Table V. Stabilization Energy of Monosubstituted Methyl Radical and Cation

R	SE $(RCH_2\cdot)$, kcal/mole	SE (RCH_2^+), kcal/mole
CN	$+11 \pm 3$	-10 ± 3
H	(0)	(0)
CH_3	9 ± 3	37 ± 3
F	13 ± 3	27 ± 3
Cl	14 ± 4	30 ± 4
Br	19 ± 5	37 ± 5
OCH_3	20 ± 3	66 ± 3

In Table V are given the stabilization energies of some monosubstituted methyl radicals and ions. The radical

stabilization by substituents with an unshared pair are one-fourth to one-half as large as the stabilization energies for the corresponding cation. This ratio is generally somewhat less (as seems reasonable[43]) than that of 1:2 which is anticipated by the relative delocalization energy from HMO calculations for 3($\ddot{X}CH_2\cdot$) and 2($\ddot{X}CH_2$) π-electron systems. If the mean observed ratio of roughly 1:3 applies to the as yet uninvestigated $\cdot CH_2N(CH_3)_2$ radical, the previously obtained SE for the ion[2] anticipates the very low dissociation energy $D[(CH_3)_2NCH_2-H] = 70$ kcal/mole.

The cyano substituent stabilizes the radical,[44] but, as indicated in Table V, this substituent has a destabilizing effect on the ion. The repulsion associated with the valence-bond structure, $^+CH_2-C^+=N:^-$, evidently exceeds any resonance stabilization derived from the structures: $^+CH_2C\equiv\ddot{N}: \leftrightarrow CH_2=C=N:^+$.

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Ion–Molecule Reactions in Liquid Hydrocarbons *via* Photoionization with Vacuum Ultraviolet Radiation. The Polymerization of Isobutene

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Abstract: The uncertainty of the effects of the catalyst fragments and solvent molecules in a conventional cationic polymerization system leads to many approximations in the kinetic description of the reaction. A system was developed which completely eliminates these variables and which leads to the simplification of the kinetic expressions. This system is comprised of an ultraviolet source capable of producing photons of sufficient energy to ionize a monomer molecule and a reaction cell in which the ionized fragments are separated by an electric field. The monomer molecules are ionized in the vapor phase and the positive ion fragments caused to drift into the liquid monomer. These positively charged fragments initiate the bulk polymerization of the monomer in the absence of counterions and solvent molecules. An extensive investigation of the isobutene system led to the postulation of molecular weight limitation by solubility of the polymer *via* a unimolecular transfer mechanism. This unimolecular transfer mechanism also explains some of the seemingly anamolous results reported in the literature for the conventional cationic polymerization of isobutene. A complete description of the apparatus is given.

Ionic polymerizations involve the attack of an ion or an ion pair on a neutral molecule. The nature of the formation of the ion pair as well as the nature of the attack on the ion are very little understood processes. Almost all investigations have been limited to a study of chemical initiation with the production of an ion pair in a liquid medium.[1-10] This does not allow one

to study primary reactions very easily, since reaction times are extremely short. Furthermore, the system is usually complicated by the presence of solvents and the unknown effect of the counterion in solution, making

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