

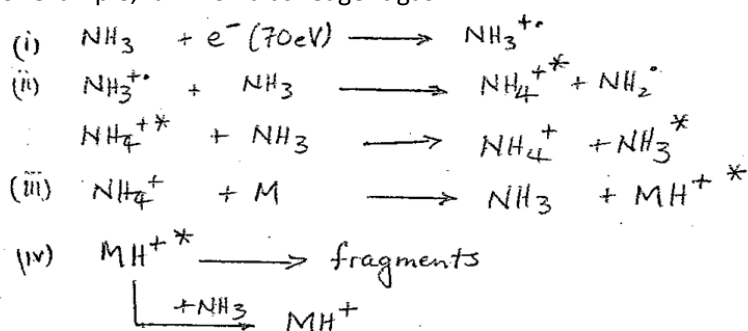
Lecture 3 Chemical Ionization (CI):

CI was introduced as a "soft" ionization method by Munson and Field in 1966 to address the problem that many molecules do not give molecular ions in EI because of fragmentation. "Quasi-molecular ions" are formed by ion/molecule reactions from an appropriate reagent ion itself generated by EI. The method is very versatile — since it depends on chemical reactions — and hence can be used to control energy deposited, achieve selective ionization, etc. The CI source contains a lightly ionized plasma so that approximately equal numbers of positive and negative ions are present, the method is good for negative ion MS either through ion/molecule reactions or through electron attachment using the thermal electrons which are present.

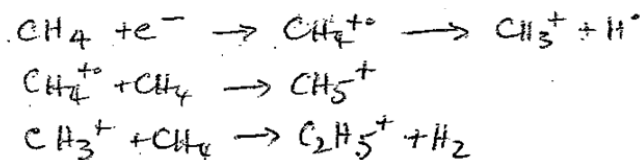
Sequence of steps:

- (i) e^- impact on reagent gas
 - (ii) ion/molecule reactions give reagent ion(s)
 - (iii) reagent ions react with analyte
 - (iv) unimolecular fragmentation or collisional cooling of ionized sample
- (To avoid direct electron ionization of the analyte, the reagent gas sample ratio is at least 100:1.)

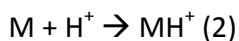
For example, -ammonia as reagent gas:



Consider the case of methane reagent gas. The optimum pressure for CI is when there is a stable population of reagent ions (invariant with pressure), This requires a certain number of collisions which is achieved by raising the pressure. The reactions involved and their pressure variation are shown:



Energy Deposition in CI



$$\begin{aligned} \Delta H_{rxn}(1) &= \Delta H_f(MH^+) + \Delta H_f(CH_4) - \Delta H_f(M) - \Delta H_f(CH_5^+) \\ &= [\Delta H_f(MH^+) - \Delta H_f(M)] - [\Delta H_f(CH_5^+) + \Delta H_f(CH_4)] \end{aligned}$$

But $PA \equiv -\Delta H_{rxn}(2)$

$$\Delta H_{rxn}(2) = \Delta H_f(MH^+) - \Delta H_f(M) - \Delta H_f(H^+)$$

$$\therefore PA = -[\Delta H_f(MH^+) - \Delta H_f(M) - \Delta H_f(H^+)]$$

\therefore Substituting and dropping common $\Delta H_f(H^+)$ terms

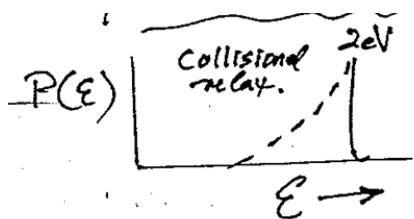
$$\Delta H_{rxn}(1) = -PA(M) - [-PA(CH_4)] = PA(CH_4) - PA(M) = -684 - 880 \text{ kJ/mol} = -200 \text{ kJ/mol} \cong -2 \text{ eV}$$

$$PA(M) = 880 \text{ kJ/mol}$$

$$PA(CH_4) = 684 \text{ kJ/mol}$$

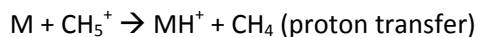
$$\Delta PA = 2 \text{ eV}$$

Most of this energy goes in ion (Larger, New bond)



Control of Internal Energy

Note that a change in the reagent ion changes the internal energy deposited. For example, for proton transfer the heat of reaction is given by the proton affinity difference between analyte and reagent gas:

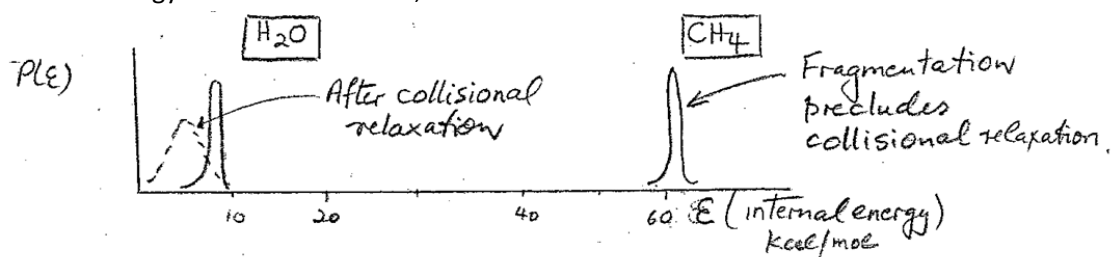


$$\Delta H_{rxn} = \Delta H_f(MH^+) - \Delta H_f(M) - [\Delta H_f(CH_5^+) - \Delta H_f(CH_4)]$$

$$PA = -[\Delta H_f(MH^+) - \Delta H_f(M) - \Delta H_f(H^+)]$$

$$\therefore \Delta H_{rxn}(\text{proton transfer}) = PA(CH_4) - PA(M)$$

For a "typical" organic compound with a proton affinity (negative of the enthalpy change on proton addition) of 180 kcal/mol, the energy made available by CH_4 is 180 - 128 kcal/mol while that made available by H_2O is 180 - 173 kcal/mol. If the excess energy is assumed to lodge in the ion (normally many more degrees of freedom than the neutral compound) then methane and water give the initial internal energy distributions shown;



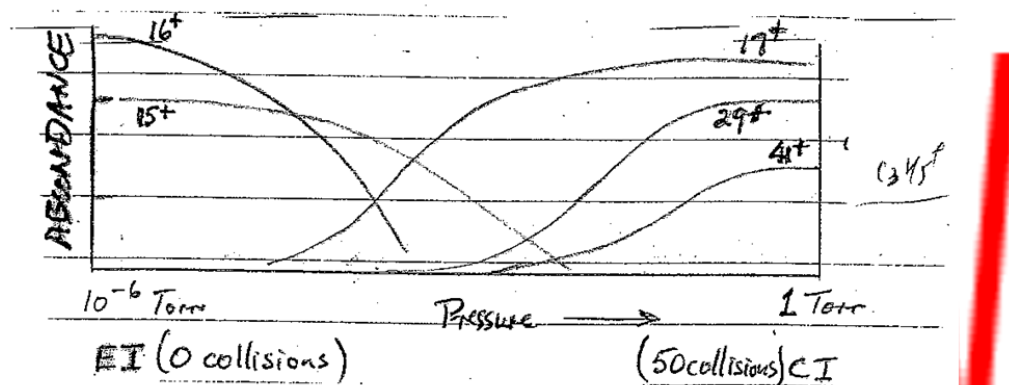
These distributions may be modified by collisions which will remove internal energy if fragmentation is slow. (Time between collisions, reciprocal of collision frequency, is ca 0.1 μ sec).

Base	Proton Affinities		Base	Proton Affinities	
	kJ/mol	kcal/mol		kJ/mol	kcal/mol
H ₂	422	101	(CH ₃) ₂ CO	823	197
O ₂	423	101	NH ₃	857	205
HF	468	112	C ₆ H ₅ NH ₂	884	211
CH ₄	536	128	CH ₃ NH ₂	894	214
H ₂ O	723	173	(CH ₃)NH	920	220
H ₂ S	738	177	Pyridine	921	220

HCN	748	179	(CH ₃) ₃ N	938	224
i-C ₄ H ₉	823	197	(CH ₃) ₂ N(CH ₂) ₂ N(CH ₃) ₂	996	238

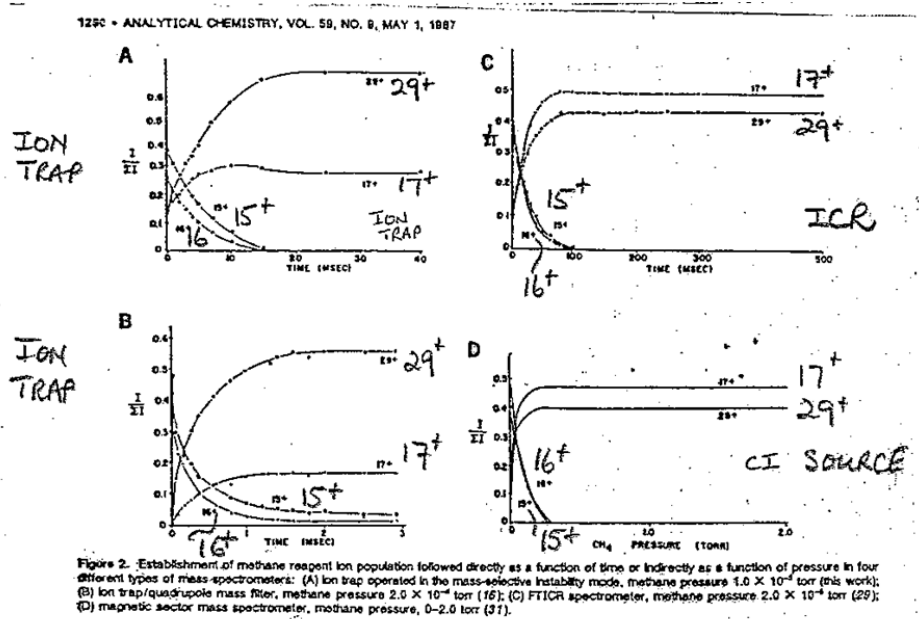
From D. H. Aue and M. T. Bowers (Ed.), *Gas Phase ion Chemistry*, Academic Press, New York, 1979, Vol.2, ch. 9

Practice of CI: # of Collisions



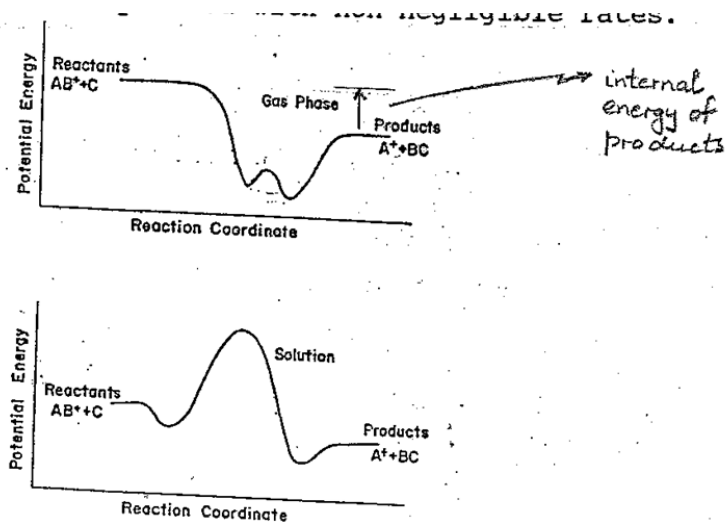
The conditions in a CI source are such that *thermal equilibrium* is achieved but *chemical equilibrium* is not. That is, ionic products are often kinetically rather than the thermodynamically favored species. It is estimated from the residence time (ca 10 μsec) and pressure (0.5 torr) that about 50 collisions usually occur. Higher pressures can be used to establish equilibrium (*high pressure mass spectrometry* ca 10 torr) or longer times can be used (eg in flowing afterglow where pressure is similar to CI source pressures but msec time scales). Less desirable is atmospheric pressure ionization since charge tends now to migrate to the most favored species, often a trace impurity (eg water) and since extensive clustering is observed — direct air monitoring is the main impetus for API studies. Note that there are some practical difficulties with operating at the CI pressure range — this is where gases conduct well and this must be considered when using high voltage instruments. Sources which can readily be switched during operation from CI to EI (mechanically or electrically) are available.

The similarity in reagent ion populations achieved by increasing time vs raising pressure are illustrated by the following data:



Ion/Molecule Reactions in CI vs. Solution

It is to be noted that the potential energy surfaces for ion/molecule reactions have the form shown and that exothermic CI reactions need collisional stabilization if the intact product is to be observed (otherwise it will revert to reactants assuming that fragmentation does not intervene). Note too that only exothermic ion/molecule reactions proceed with non-negligible rates.

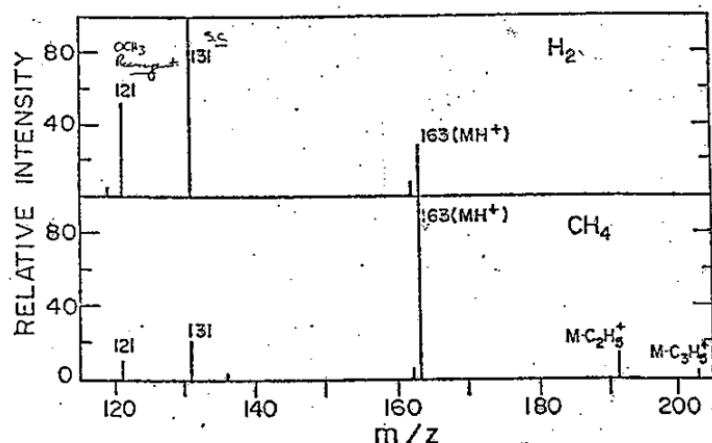


Adduct ions in CI

An example of the effect of changing reagent ton on CI spectra is:

Methyl cinnamate $\text{PhCH}=\text{CH}-\text{C}(\text{O})-\text{OCH}_3$ MW=162

$\text{PA}(\text{CH}_4) - \text{PA}(\text{H}_2) = 27 \text{ kcal/mol}$ [Harrison](#)



Note: 1) Internal energy effect (fragments) 2) adducts (ion/molecule reaction products)

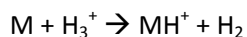
Back to Thermochemistry

The proton affinity (PA) is an enthalpic quantity that measures the strength of binding of the proton to a neutral molecule (eq. 13-10). The PA of H₂ is low, only

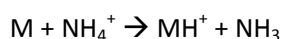
$\text{PA} \equiv -\Delta H_{\text{reaction}}$ for the reaction: $\text{H}^+ + \text{M} \rightarrow \text{MH}^+$

422 kJ mol⁻¹ (101 kcal mol⁻¹) compared to 854 kJ mol⁻¹ (204 kcal mol⁻¹) for NH₃. Hence proton transfer from H₃⁺ to NH₃ is exothermic by the difference between these values, or 432 kJ mol⁻¹ (103 kcal mol⁻¹).

Organic amines have proton affinities on the order of 900 kJ mol⁻¹ (215 kcal mol⁻¹) and can be ionized using either hydrogen or ammonia as reagent gases, but with vastly different consequences:



$$\begin{aligned} \Delta H_{\text{reaction}} &= - (900 - 422 \text{ kJ mol}^{-1} \text{ or } 215 - 101 \text{ kcal mol}^{-1}) \text{ (13-11)} \\ &= - 478 \text{ kJ mol}^{-1} \text{ or } -113 \text{ kcal mol}^{-1} \end{aligned}$$



$$\begin{aligned}\Delta H_{\text{reaction}} &= - (900 - 854 \text{ kJ mol}^{-1} \text{ or } 215 - 204 \text{ kcal mol}^{-1}) \text{ (13-12)} \\ &= - 46 \text{ kJ mol}^{-1} \text{ or } -11 \text{ kcal mol}^{-1}\end{aligned}$$

The excess energy of the protonation reaction using H_2 reagent is almost 500 kJ mol^{-1} ($120 \text{ kcal mol}^{-1}$). It lodges principally in MH^+ and causes extensive dissociation. In the case of NH_3 reagent, the exothermicity is less than 50 kJ mol^{-1} (12 kcal mol^{-1}). This value is less than typical bond energies and is insufficient to cause dissociation. As a result, H_2 is appropriately described as a hard ionization reagent, which produces extensive fragmentation and leaves few or no intact protonated molecules to be observed. Ammonia is a soft reagent and produces principally the intact protonated molecule of the organic amine. Proton affinities of a variety of simple organic compounds are listed the Table A-3. With these data; it is possible to predict whether a particular analyte—reagent ion combination will lead to mild or extensive fragmentation.

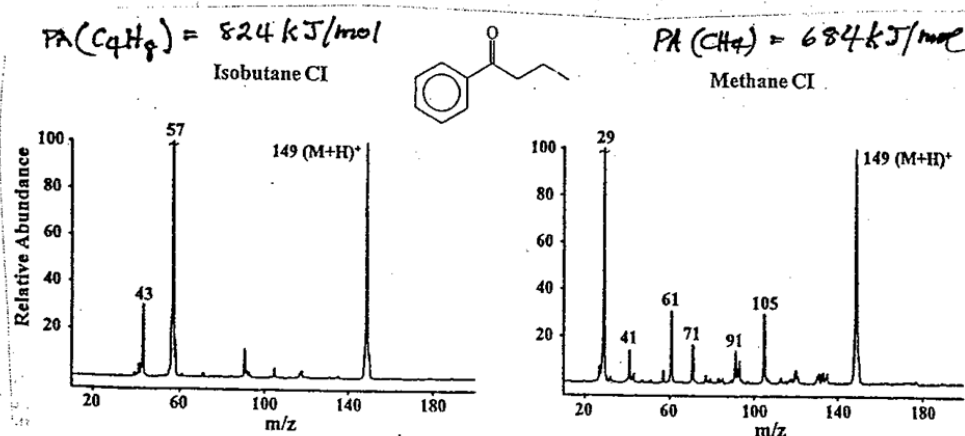


Figure 13-7 Control of degree of fragmentation of phenyl propyl ketone made possible by choice of chemical ionization reagent gas.

Reagent Gas Choice: Reagent Ions

A change in the reagent ion can also be used to change the nature of the ionic product, so that hydride abstraction, electron (charge) transfer, metal atom transfer, methylation, etc can be achieved. The table shows some common reagents and the reactions they produce.

TABLE 11-10 Some Chemical Ionization Reagents

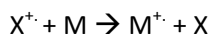
TABLE 11-10 Some Chemical Ionization Reagents

Reagent Gas	Reagent Ion	Analyte Ion	Comment
H ₂	H ₃ ⁺	(M+H) ⁺	very energetic, considerable fragmentation
CH ₄	CH ₅ ⁺	(M+H) ⁺	energetic protonating agent
CH ₄	C ₂ H ₅ ⁺ , C ₃ H ₅ ⁺	(M+C ₂ H ₅) ⁺ (M+C ₃ H ₅) ⁺	form adduct ions
<i>i</i> -C ₄ H ₁₀	C ₄ H ₉ ⁺	(M+H) ⁺	mild protonating agent, ionizes all nitrogen bases
NH ₃	NH ₄ ⁺	(M+NH ₄) ⁺	selective; little fragmentation
NH ₃ -CH ₄	NH ₄ ⁺	(M+H) ⁺	selective protonating agent
Biacetyl	CH ₃ CO ⁺	(M+CH ₃ CO) ⁺	acetylating agent
Ar	Ar ⁺	M ⁺	energetic charge exchange agent
CS ₂	CS ₂ ⁺	M ⁺	mild charge exchange agent
CH ₃ ONO-CH ₄	CH ₃ O ⁻	(M-H) ⁻	mild proton abstraction reagent
NF ₃	F ⁻	(M-H) ⁻	proton abstraction reagent
CHCl ₃ -CH ₄	Cl ⁻	(M+Cl) ⁻	chloride addition reagent

Table 1-5 Reactions Used in CI

Reaction	Reagent	Reagent Ion	Product	Thermochemical Property
Proton transfer	<i>i</i> -C ₄ H ₁₀	C ₄ H ₉ ⁺	(M+H) ⁺	Proton Affinity
Charge exchange	Ar	Ar ⁺	M ⁺	Ionization energy
Electron attachment	CH ₄	e ⁻	M ⁻	Electron affinity
Cl attachment	CHCl ₃ /CH ₄	Cl ⁻	M+Cl ⁻	Cl ⁻ affinity
Metal ion attachment	Ag	Ag ⁺	(M+Ag) ⁺	Ag affinity
Adduct formation	Biacetyl	CH ₃ CO ⁺	(M+CH ₃ CO) ⁺	Acetyl affinity
Cluster ion formation	Py	PyH ⁺	(M+Py+H) ⁺	Molecular Pair Affinity

Charge Exchange



Thermochemistry: Reaction only occurs at low KE if exothermic,

$$\Delta H_{\text{reaction}} = \Delta H_f(X) + \Delta H_f(M^+) - \Delta H_f(X^+) - \Delta H_f(M^+)$$

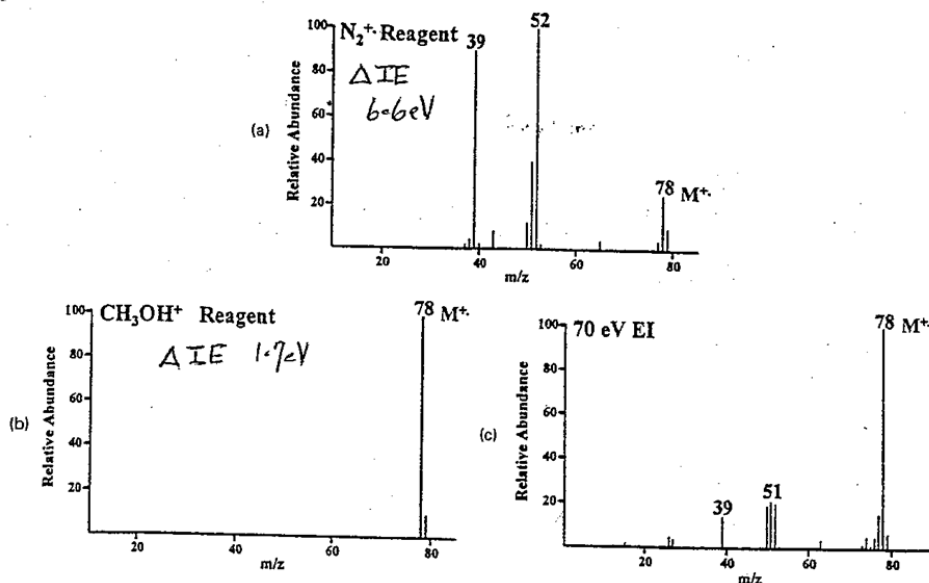
$$\text{but } IE(X) = \Delta H_f(X^+) - \Delta H_f(X) \quad \Delta H_f(e^-) \cong 0$$

$$\therefore \Delta H_{\text{reaction}} = IE(M) - IE(X)$$

If $IE(M) < IE(X)$, excess energy is assumed to go to M (polyatomic), i.e. $P(\epsilon) = IE(X) - IE(M)$

Use atomic or simple reagent ions such as CS_2

An experiment which illustrates the type of fragmentation which occurs upon CE is shown below. Note that the EI mass spectrum (70eV) has features of both these spectra consistent with the broad internal energy distribution in which both low internal energy and high internal energy ions are represented.



Charge exchange CI mass spectra of benzene (IE 9.2 eV) recorded using hard and soft reagents (N_2 and CH_3OH as reagent gases), compared with the 70 eV EI mass spectrum. The molecular ion (M^+) is generated with a large amount of internal energy from N_2^+ (IE 15.8 eV) compared with CH_3OH^+ (IE 10.9eV).

Negative Ion-Chemical Ionization (NCI)

Two fundamentally different types of reactions:

- ❖ based on ion/molecule reactions
- ❖ based on electron/molecule processes

Differences are speed of the reactions ($\times 1000$)

Bronsted acid/base CI chemistry are fundamentally similar even if polarities are different,

Hence energy deposition depends on energy of proton transfer in both cases, even though it is ΔPA in one case and ΔH_{acid} in the other.

Similarly adduct formation with positive and negative ions is fundamentally similar (e.g. $[M + CH_3]^+$ vs. $[M + Cl]^-$ using reagents methane and chloroform, respectively) Since both must be stabilized by collisions otherwise they will fragment.

However, electron attachment, the second type of negative ion CI experiment is different: it is necessarily a resonance process; it is very fast; the thermochemical property involved is electron affinity but it is weaker than expected since vertical values dominate fast processes and differ strongly from adiabatic; also attachment can be temporary; etc.

In these and other ways formation of M^- is much unlike the formation/properties of the analogous species M^+ .

Table 13-10 Some Reagents Used in Negative Ion and Electron Capture CI

Reagent Gas	Reagent Ion/ e^-	$PA(X)^* \text{ kJ mol}^{-1}$
NH_3	NH_2^-/e^-	1689
CH_4	e^-	
CH_4 and N_2O or CH_4 , N_2O and He or H_2 , N_2O and He	OH^-	1635

N ₂ O or N ₂ O + N ₂	O ⁻	1599
CH ₄ (at 1 torr) + 0.1% methyl nitrite	CH ₃ O ⁻	1592
CH ₃ O ⁻ + CH ₃ CN	CH ₂ CN ⁻	1560
NF ₃ (0.1 torr) or CHF ₃	F ⁻	1554
O ₂ (1 torr, Townsend discharge) or mixture of (O ₂ and H ₂)	O ₂ ⁻	1476
F ⁻ + CH ₃ CH ₂ CN	CN ⁻	1469
OH ⁻ + CH ₃ COOCH ₃	CH ₃ CO ₂ ⁻	1459
CH ₂ Br ₂	Br ⁻	1356
CH ₂ Cl ₂ or CHCl ₃ or CF ₂ Cl ₂ or (CH ₂ Cl ₂ + CH ₄)	Cl ⁻	1395

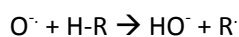
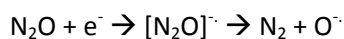
* Proton affinity of X anion (4.18 kJ mol⁻¹ = 1 kcal mol⁻¹).

The negative ion Cl experiments can use an enormous variety of reagents chosen, as in positive ion Cl, to deposit more or less internal energy into the product ion. Some choices of proton abstraction reagents are shown in the table which follows:

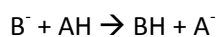
Reagent Gas	Reagent Ion	Product Ion
CH ₄ /CH ₃ ONO (100:1)	CH ₃ O ⁻	(M-H) ⁻
CH ₄ /N ₂ O	HO ⁻	(M-H) ⁻
N ₂ O	O ⁻	(M+O) ⁻

CH₃NO₂ EA = +0.44 eV

Some common NCI reactions are



Bronsted base Cl

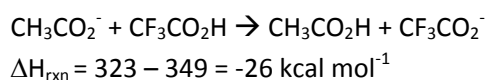


$PA(A^-) \equiv \Delta H_{acid}(HA)$ exothermic, hence measure rate, if $PA(B^-) > PA(A^-)$ or if AH is a stronger acid than BH [expressing it in ΔG terms] i.e. if $\Delta G_{acid}(BH) > \Delta G_{acid}(AH)$

$(\Delta H_{acid} = \Delta H \text{ AH} \rightarrow A^- + H^+) \quad (PA(A^-) = -\Delta H \text{ A}^- + H^+ \rightarrow AH)$
 e.g. acetic acid, $\Delta H_{acid} = 349 \text{ kcal mol}^{-1}$

is a strong acid and its conjugate base, acetate will only deprotonate even stronger acids (stronger acids have lower ΔH_{acid}) e.g. CF_3CO_2H , $\Delta H_{acid} = 323 \text{ kcal mol}^{-1}$

viz. $\Delta H_{acid}(CH_3CO_2H) = 349 \text{ kcal mol}^{-1} > \Delta H_{acid}(CF_3CO_2H) = 323 \text{ kcal mol}^{-1}$



$$\Delta H_{rxn} = \Delta H_{acid}(AH) - \Delta H_{acid}(BH)$$

Common reagent OH^- : gives $(M-H)^-$ often little fragments

Cl^- : weak base $\Delta H_{acid} = 333 \text{ kcal mol}^{-1}$ (HCl strong acid)

Some Gas Phase Acid Strengths (Enthalpies)* $\Delta H_{acid}(AH) \equiv PA(A^-)$

Compound	$\Delta H_{acid}(\text{kcal mol}^{-1})$	$\Delta H_{acid}(\text{kJ mol}^{-1})$
CH ₄	417	1743
NH ₃	404	1689
H ₂	400	1672
H ₂ O	391	1634
CH ₂ =CHCH ₃	391	1634
CH ₃ OH	381	1593
C ₂ H ₂	379	1584
HF	372	1555
(CH ₃) ₂ CO	370	1547
PH ₃	368	1540

CH ₃ SH	357	1494
H ₂ S	351	1469
CH ₃ CO ₂ H	349	1460
HCl	333	1393
HBr	324	1356
CF ₃ CO ₂ H	323	1352
HI	314	1314

*Data from S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, D. R. Levin, and W.G. Mallard, Gas Phase Ion and Neutrals *J. Phys. Chem. Ref. Data*, 17, (S)1 (1988).

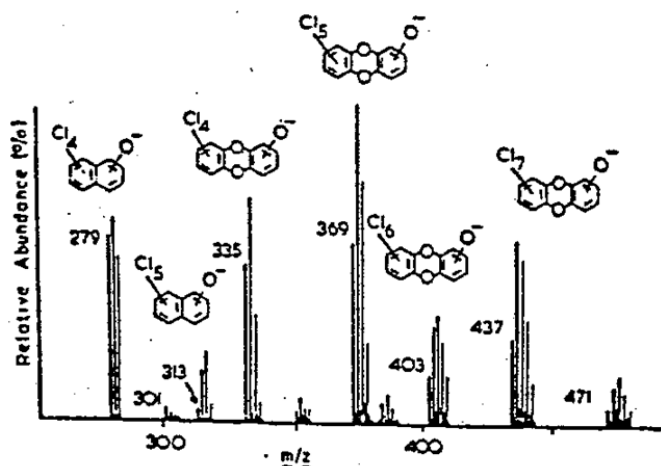
Enthalpies defined for $\text{HA} \rightarrow \text{A}^- + \text{H}^+$ as $\Delta H_{\text{acid}}(\text{HA}) = \Delta H_f(\text{A}^-) + \Delta H_f(\text{H}^+) - \Delta H_f(\text{HA})$

Negative Ion Chemical Ionization

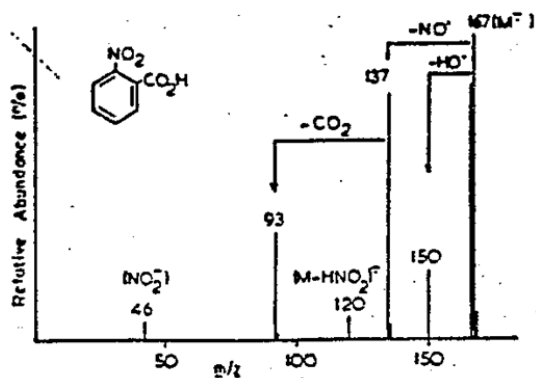
In contrast to negative ion EI, gives good intensities. There are two experiments

- A) those in which the electron is the reagent ie electron attachment or dissociative attachment or pair formation and
- B) those in which some other negative ion is the reagent. The latter is completely analogous to positive ion CI. (There are approx. equal no's of positive and negative ions in CI plasma).

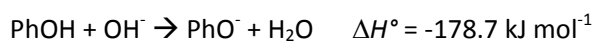
The electron attachment experiments employ the CI reagent as a buffer gas to reduce electron energy (methane, isobutane and nitrogen are common). A functional group with high electron affinity is added to the molecule - eg pentafluorophenyl, penta or heptafluorobenzyl, etc. The high electron mobility increases the rate of the attachment reaction and makes the method extremely sensitive more so than any other gas phase ionization method, and ca x 100 more than positive EI and conventional positive or negative CI.



Cl (electron attachment)



Thermochemistry



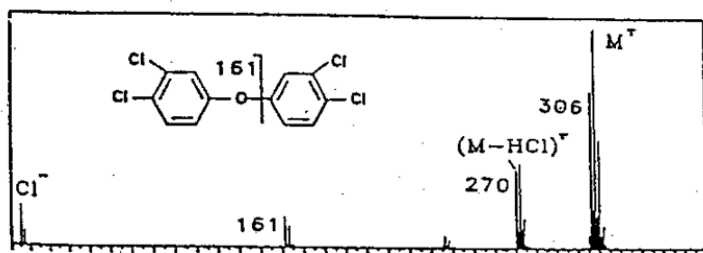
Negative ions: cold Positive Ions: hot

The exothermicity of the reaction is the result of the formation of H_2O , which is neutral and carries off the excess energy. The product anion will be 'cold'.

However, during a positive ionization, the following will occur:

In this case, the exothermicity comes mainly from the association of the proton with the molecule to be ionized. The resulting cation will contain an appreciable level of excess energy.

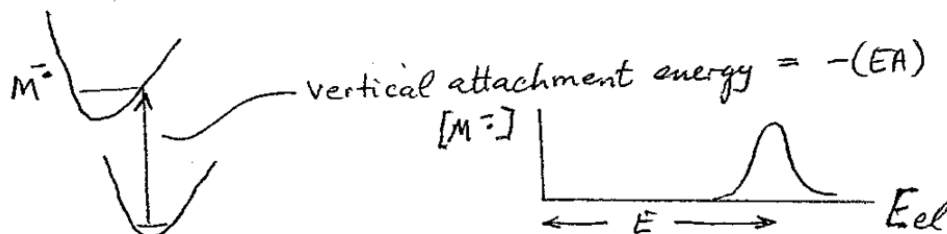
Electron attachment (electron capture) CI



Electron attachment chemical ionization mass spectrum of 3,3',4,4'-tetrachlorodiphenyl ether methane to moderate electron energies (ion source temperature=250 °C) (Stemmler and Hites, 1988)

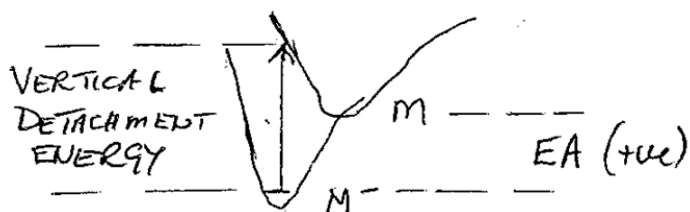
Thermochemical Information

Electron affinities can be determined in electron capture experiments if a resonance peak occurs in the plot of ion abundance vs electron energy, ie if the EA value is negative. The quantity measured is actually a *vertical attachment energy* and it is the negative of the vertical EA. As usual the adiabatic values are not measured. However, the error is much greater than in IE's where differences in Franck—Condon factors tend to be smaller. The addition of an electron to a LUMO changes the energy of all the other orbitals substantially - this reorganization energy is the energy which is ignored in Koopman's theorem which equates orbital energy with energy for electron removal.



Dissociative electron capture also can be used to yield electron affinities if all the other quantities are known, viz, like AE it gives a heat of formation value for the anion, but is subject to similar problems to those in getting good cation heats of formation from AE values.

$$AB + e^- \rightarrow A^- + B \quad KE_{e^-} = \Delta H_{rxn} = \Delta H_f(A^-) + \Delta H_f(B) - \Delta H_f(AB)$$



Photodetachment is a precise method of determining electron affinities (again, the vertical quantities)

Positive/negative Desorption Chemical Ionization I

Desorption chemical ionization (DCI) is a hybrid between CI, which requires that the sample be vaporized, and the DI techniques, discussed later, which require energetic bombardment of the condensed phase sample. DCI works well for both positive and negative ions. The advantage of DCI is that samples of low volatility can be examined using simple apparatus. The data in Figure 13-9 were recorded by DCI. Its applicability to nonvolatile samples is illustrated by the case of thymidylyl(3'-5')thymidine methyl phosphotriester, the positive and negative DCI spectra of which are shown in Figure 13-10. Note that the reagent used in this experiment, NH_3 , can serve to thermalize electrons and so act as an electron capture reagent, or it can serve as a proton

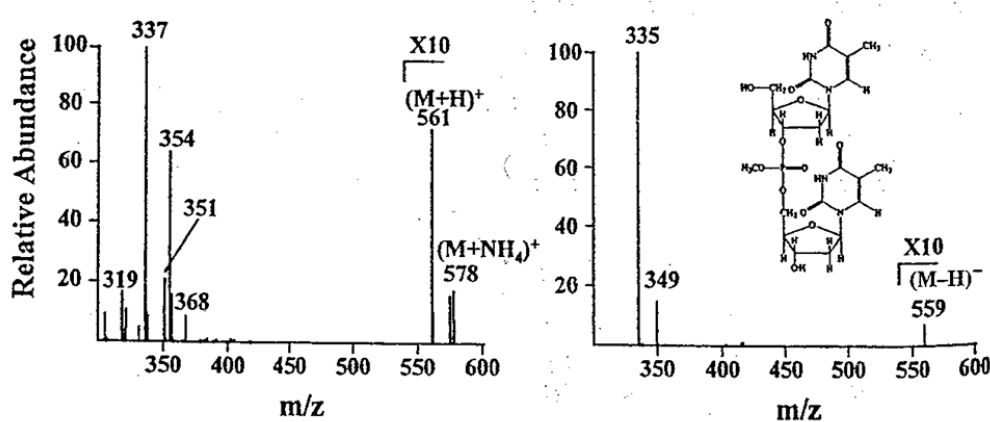
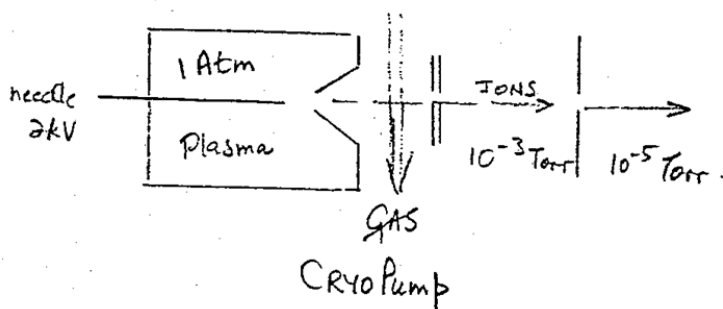


Figure 13-10 Positive and negative ion desorption CI (DCI) mass spectra of a methylated dinucleotide, ammonia reagent gas, showing various forms of the molecular ion. (From I. Isern-Flecha et al., *Biomed. Environ. Mass Spectrom.* 14, 17, [1987]. Reproduced with the permission of John Wiley & Sons Ltd., Chichester, UK.)

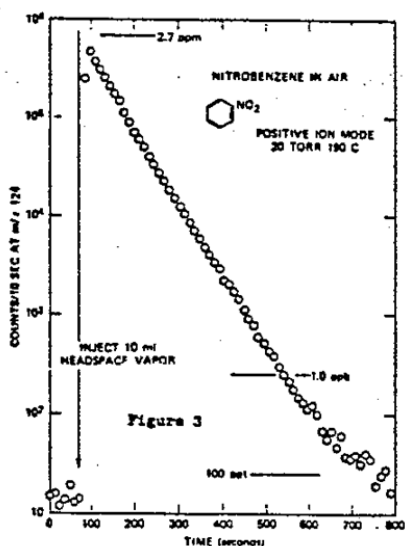
Atmospheric pressure ionization (See *Anal. Chem.* 1983, 1485A)

This variant on the CI experiment uses either a corona discharge or a beta emitter instead of a filament. It is common to use "standard" air as support gas to minimize charges in amounts of trace basic or acidity compounds since these tend to accumulate the charge in the form of protonated or deprotonated cluster ions. The method is extremely sensitive to these types of compounds but there are strong matrix effects. An excellent interface is the "gas curtain" which uses fluid dynamics to allow only ions to penetrate from the atmospheric pressure source to the vacuum of the analyzer. The result is a

very clean system. Cluster ions can be declustered in a "cluster buster" or collision region.



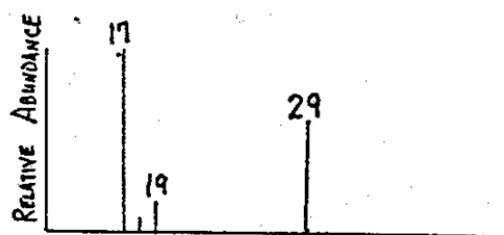
An example of the trace analysis capability is shown by the detection in the positive ion mode of nitrobenzene in air down to 100 ppt.



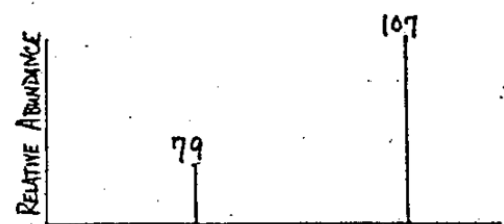
The sensitivity data presented here were obtained by injecting a known Volume of of headspace vapor of the test substance into 1-liter exponential dilution flask. The air flow through the flask was approximately 1 liter/min and a portion of this was sampled at one atmosphere into the flowing discharge ion source.

CI with mass selected reagent ions

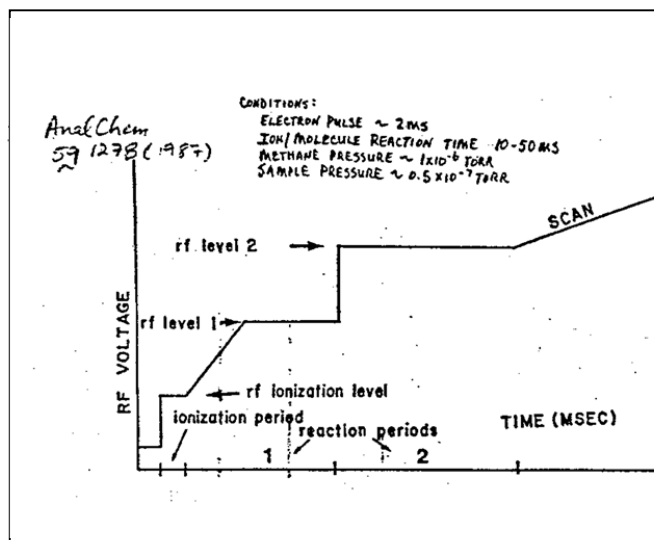
As normally practiced a mixture of reagent ions may be formed in the CI source. In some cases use of just one ion is desirable and this is achievable in an MS/MS experiment. A particularly simple way of achieving this is to use an ion trap. The type of result obtained and the scan sequence used is illustrated in the case of benzaldehyde:



METHANE REAGENT IONS



CI OF BENZALDEHYDE (M.WT. 106)



Some CI Reagent Gases and Reagent Ions (Proton Transfer Reactions)

Reagent Gas	Reagent Ion	Analyte Ion	Comment
H ₂	H ₃ ⁺	(M+H) ⁺	Very energetic protonating agent produces considerable fragmentation
CH ₄	CH ₅ ⁺ , C ₂ H ₅ ⁺ , C ₃ H ₅ ⁺	(M+H) ⁺ , (M+C ₂ H ₅) ⁺ , (M+C ₃ H ₅) ⁺	Energetic protonating agent, forms adduct ions
<i>i</i> -C ₄ H ₁₀	C ₄ H ₉ ⁺	(M+H) ⁺ , (M+C ₄ H ₉) ⁺	Mild protonating agent; ionizes all nitrogen bases
NH ₃	NH ₄ ⁺	(M+NH ₄) ⁺ , (M+H) ⁺	Selective ionization, little fragmentation
NH ₃ /CH ₄	NH ₄ ⁺	(M+H) ⁺	Selective protonating agent
CH ₃ ONO/CH ₄	CH ₃ O ⁻	(M-H) ⁻	Mild proton abstraction reagent
NF ₃	F ⁻	(M-H) ⁻	Proton abstraction reagent

Reactions Used in CI

Reaction	Reagent*	Reagent Ion*	Product	Thermochemical Property

Proton transfer	<i>i</i> -C ₄ H ₁₀	C ₄ H ₉ ⁺	(M+H) ⁺	Proton affinity
Charge exchange	Ar	Ar ^{+•}	M ^{+•}	Ionization energy
Electron capture	CH ₄	e ⁻	M ^{-•}	Electron affinity
Cl ⁻ attachment	CHCl ₃ /CH ₄	Cl ⁻	(M+Cl) ⁻	Cl affinity
Adduct formation	Biacetyl	CH ₃ CO ⁺	(M+CH ₃ CO) ⁺	Acetyl affinity
Cluster ion formation	Py	PyH ⁺	(M + Py + H) ⁺	Molecular pair affinity

*Examples given are typical cases; many other choices can be made.

Summary of Characteristics of CI

Sample must be volatile	Limited to sample molecular weight approximately 800 Da or less
Hard or soft ionization	Molecular weight determination or fragmentation for structural information
Variety of ionization processes	Multiple checks of molecular weight, structural features
Universal or selective method	Either is available, depending on choice of reagent gas
Negative ions are readily formed	Additional tool for molecular weight and structural and thermochemical measurements

