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Stabilization Energy and Ion Size in Carbocations in the Gas Phase

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Abstract: Stabilization in even-electron carbocations, R^+, as measured by the heterolytic bond dissociation energy, $D(R^+-H^-)$, depends primarily on the size of the ion. For classes of ions having common structural features, e.g., primary, secondary, and tertiary alkyl ions and allylic, allenic, and aromatic carbonium ions, $D(R^+-H^-)$ is a linear function of the logarithm of the number of atoms in R^+. Ions which do not obey these simple relationships (e.g., the 2-norbornyl cation) possess special structural features. No overall relationship appears to exist between stabilization effects in ions and in the corresponding free radical.

In earlier work we have shown that the heats of formation of gaseous molecular positive ions in homologous series decrease systematically with increasing size of the ion, and can be reproduced, generally to within 1–2 kcal mol^{-1}, by using a very simple formula.[1] Appropriate correction terms were derived to allow for chain branching and double-bond position, similar to those used in additivity schemes for the heats of formation of neutral molecules.[2] In a second paper[3] consideration was given to ionic series resulting from multiple substitution by characteristic groups CH_3, OH, and OCH_3 on charge-bearing atoms. For these ions good straight-line relationships between ΔH_f(ion) and the logarithm of the number of atoms (i.e., size) were found. The slopes of the lines for multiple substitution of each substituent were approximately constant, provided that the substitution was at a C atom on which the positive charge may be formally located, that is, at a double-bonded C atom or "starred" C atom in a delocalized π system. As seems reasonable, substitution of CH_3 groups[3] or OH groups[4] on C atoms remote from double bonds, or on "unstarred" C atoms in π systems, causes little or no change in stabilization, the change in heat of formation now being essentially the same for the ion and the neutral. That is, these substitutions have no effect on the ionization energy of the radical or molecule.

The effect of group substitution on the stabilization energy of hydrocarbon free radicals is usually expressed in terms of the decrease in *homolytic bond dissociation energy*, $D(R-H)$, with respect to the reference value $D(CH_3-H)$. By analogy, the most useful way of quantifying the stabilization energy for ions is by the decrease in the *heterolytic bond dissociation energy* or hydride ion affinity, $D(R^+-H^-)$. The gas-phase stabilization energy E_s for an ion R^+ is then given by $D(CH_3{}^+-H^-) - D(R^+-H^-)$. The effect of group substitution on E_s has been briefly investigated by a number of authors[3-8] from gas-phase heats of formation. A related body of data comes from the very extensive kinetic studies of solvolytic reactions in the liquid phase, which has provided most of our present knowledge of the overall effects of substituent groups in lowering the energy of an incipient carbonium ion center by charge delocalization. However, it is not possible to relate these results quantitatively to the gas-phase data because of solvation and steric effects on the reaction rates. Because of their freedom from these complicating factors, gas-phase data simplify the task of separating out the purely enthalpic effects of substitution. The relationship between the liquid-phase and gas-phase data has been recently discussed by Saluja and Kebarle[9] with respect to the stability of the 2-norbornyl ion.

Table I. Homolytic and Heterolytic Bond Dissociation Energies (kcal mol^{-1})

radical R	$D(R-H)$	ref	$\Delta H_f(R^+)$	ref	$D(R^+-H^-)^{a,b}$
CH_3	105	24	261	25	313
C_2H_5	100	26	216	14	271
n-C_3H_7	100	26	208	7	268
s-C_3H_7	96	26	192	14, 27	252
t-C_4H_9	93	26	166	14	233
allyl	87	24	226	27, 28, 29	256
propargyl	89	24, 30	281	28	271
cyclopentadienyl	82	24	255	19b	258
phenyl	111	24	279	31	294
benzyl	88	24	215	32	238
formyl	87	24	196	33	257
acetyl	86	24	156	34	230
C_2H_5CO	87	24	144	25	224
C_6H_5CO	87	24	168	35	212
$HC{=}CO$	92	30	262	36	308
CH_2CN	95	24	286	37	305
H_2N	107	24	300	25	276
CH_3NH	100	24	199	36	239
CH_2NH_2	94	24, 39	178	8	218
CH_3NHCH_2	87	39	166	8	205
CH_3CHNH_2	90	39	157	8	203
CH_3O	104	24	$\sim$198	40	$\sim$281
$HC{\equiv}CCH_2O$	100	30	227	41	252
C_6H_5O	86	24	208	36	266
CH_2OH	94	24	169	43	252
CH_3CHOH	92	24, 30	139	43	230
$(CH_3)_2COH$	91	24	120	43	220

[a] ΔH_f(RH) from ref 38 or by additivity, ref 2. [b] $\Delta H_f(H^-) = 34.7$ kcal mol^{-1}.

It is clear from the gas-phase data so far available that structural changes bring about changes in stabilization energy which are much greater in ions than in free radicals.[3-8] In the present work we have collected and expanded the range of available gas-phase data on E_s and have sought again for useful generalizations relating ion structures and enthalpies.

Experimental Section

Ionic heats of formation reported here are selected values from the recent literature, either from appearance energy (AE) or proton affinity (PA) data. Where modern values are not available, we have obtained

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(1) Holmes, J. L.; Fingas, M.; Lossing, F. P. *Can. J. Chem.* **1981**, *59*, 80.

(2) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; John Wiley and Sons: New York, 1976.

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(4) Holmes, J. L.; Lossing, F. P.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 133.

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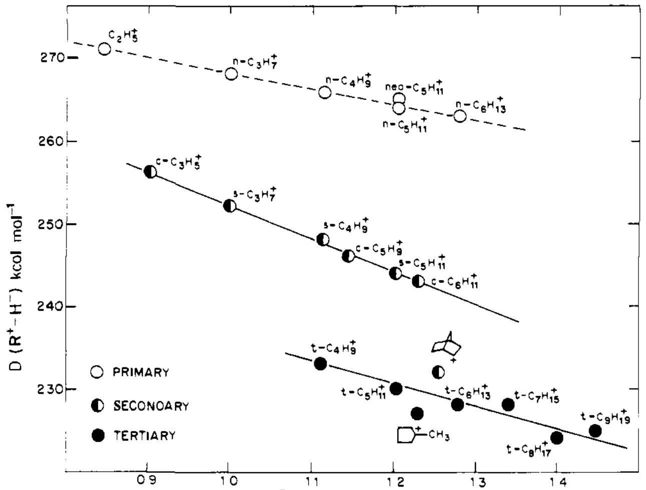

Figure 1. Heterolytic bond strengths in alkanes yielding primary, secondary, and tertiary alkyl cations as a function of log (number of atoms in the ion).

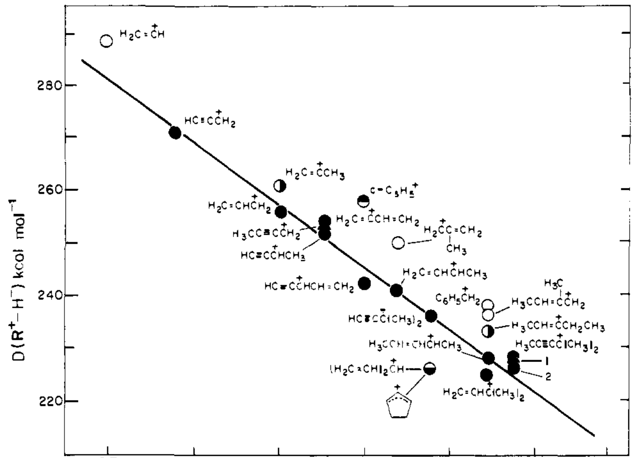

Figure 2. Heterolytic bond strengths in olefines and acetylenes as a function of log (number of atoms in the ion): (1) [cyclohexenyl]$^{+}\cdot$; (2) [methylcyclopentenyl]$^{+}$.

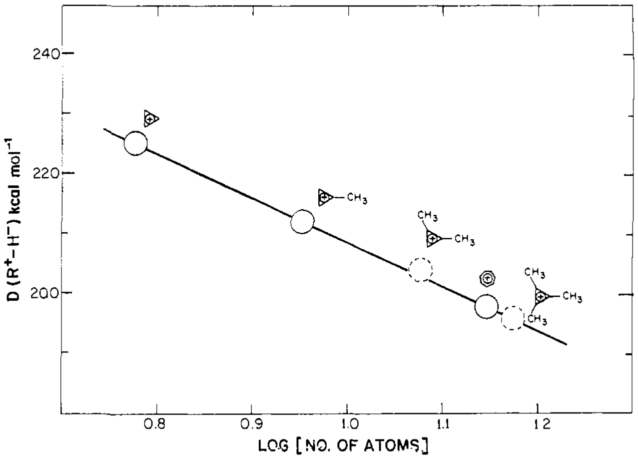

Figure 3. Heterolytic bond strengths in hydrocarbons which yield aromatic ions as a function of log (number of atoms in the ion).

Table II. Thermochemical Values for Alkyl Ions (kcal mol^{-1})

structure	$\Delta H_f(R^+)$	ref	$D(R^+-H^-)$[a]
CH_3	261	25	313
C_2H_5	216	14	271
n-C_3H_7	208	7	268
n-C_4H_9	201	7	266
n-C_5H_{11}	194	7	264
neo-C_5H_{11}	190	7	265
n-C_6H_{13}	189	7	263
s-C_3H_7	192	14, 27	252
c-C_3H_5	234	44	256
s-C_4H_9	183	7, 45	248
c-C_5H_9	193	13	246
s-C_5H_{11}	174	46	244
c-C_6H_{11}	179	47	243
2-norbornyl	185	b	232
t-C_4H_9	166	14	233
t-C_5H_{11}	159	48	230
t-C_6H_{13}	152	48	228
t-CH_3-c-C_5H_8	167	13	227
t-C_7H_{15}	147	49	228
t-C_8H_{17}	139	50	224
t-C_9H_{19}	133	51	225

[a] ΔH_f(RH) from ref 38. $\Delta H_f(C_9H_{20}) = -57.2$ kcal mol^{-1} by additivity (ref 2). [b] See text.

heats of formation from appearance energies measured by impact of an energy-resolved electron beam. The electrostatic energy selector, quadrupole mass spectrometer, and associated equipment have been described.[10,58] For those ions which rearrange to more stable isomers during the dissociative ionization process, appearance energies of fragment ions may be misleading. For such ions, particularly for $[C_4H_5]^+$ and $[C_5H_7]^+$ ions, we have preferred to obtain ionic heats of formation by direct ionization of the free radicals, together with the known or estimated heats of formation of the neutral radicals. The radicals were produced by thermolysis of the corresponding nitrites, RCH_2ONO, at ~300 °C in a tubular quartz furnace.[10,11]

Results and Discussion

Before considering structural effects on $D(R^+-H^-)$, it should be pointed out that we can find no systematic relationship between substituent effects on homolytic and on heterolytic bond dissociation energies (except for the not very useful observation that the latter are roughly 2–3 times the former). The data in Table I illustrate the absence of a useful relationship; for example, a variety of group substitutions in the formyl radical causes no change in D(R–H), whereas $D(R^+-H^-)$ ranges over 45 kcal mol^{-1}. Other series based on methyl substitution in CH_3, CH_2OH, and CH_2NH_2 are included in the table. Although for these four series D(R–H) and $D(R^+-H^-)$ are internally roughly proportional to one another, the proportionality constant for the substitution effect is different for each series. It is clear, therefore, that stabilization in ions is based upon a quite different mechanism than that in neutrals. In view of the strong effect of size on ionic heats of formation, mentioned above, the effect of size may also be a controlling one in series having a common structural feature. It is evident from Figures 1–3 that this is indeed so.

Alkyl Ions. From Table II and Figure 1 it can be seen that $D(R^+-H^-)$ for alkanes yielding primary, secondary, and tertiary ions have characteristic non-overlapping ranges of values and that for each series $D(R^+-H^-)$ decreases exponentially with the total number of atoms, that is, size. It should be noted that $\Delta H_f(R^+)$ values for primary C_3 and higher primary ions are not obtained from appearance energies because of rapid rearrangement during the dissociation process to yield secondary ions. The $\Delta H_f(R^+)$ values reported are therefore those obtained from the ionization energies of the free radicals. Theoretical calculations show that these primary alkyl ions do not have a stable minimum on the potential energy hypersurface.[12] Consequently these $\Delta H_f(R^+)$ values cannot be adiabatic values. Nevertheless, the trend in $D(R^+-H^-)$ with size is clear, although the correct slope may for this reason be significantly larger. Thus size continues to be an important parameter in stabilization, even for relatively large ions.

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(10) Maeda, K.; Semeluk, G. P.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 395.

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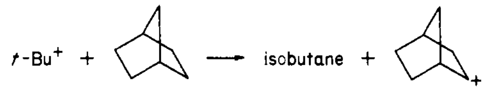
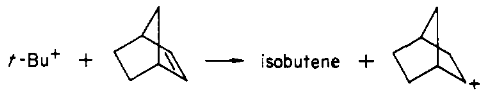
Obviously the charge must be distributed over the whole ion, and it is not localized in the formal charge site and its immediate neighbours as in a formally "classical" structure. There is an effect of delocalization beyond that of closest neighbor hyperconjugation.

Secondary and tertiary ions show a similar but larger decrease in $D(R^+-H^-)$ with increasing size. It is interesting to note that cyclic secondary ions have $D(R^+-H^-)$ values consistent with acyclic ions; although the ionic heats of formation of the former are considerably higher, the difference in $\Delta H_f(R^+)$ is offset by higher values for $\Delta H_f(RH)$.

Of particular interest is the $D(R^+-H^-)$ value for the nominally secondary 2-norbornyl ion. There are several values for $\Delta H_f[\text{2-norbornyl}]^+$ in the literature. For the reaction



Solomon and Field[13] found ΔH to be -5 kcal mol^{-1}, corresponding to $\Delta H_f[\text{2-norbornyl}]^+ = 184.5$ kcal mol^{-1} (based on $\Delta H_f[t\text{-Bu}]^+ = 166$ kcal mol^{-1}).[14] Saluja and Kebarle[9] measured for ΔH for the reaction



to be -4.3 kcal mol^{-1}. With use of $\Delta H_f[t\text{-Bu}]^+ = 166$ kcal mol^{-1} and the most recent value[15] for $\Delta H_f(\text{norbornene}) = 21.8$ kcal mol, this result gives $\Delta H_f[\text{2-norbornyl}]^+ = 187.8$ kcal mol^{-1}, in fair agreement with the result of Solomon and Field. We have measured the appearance energies for $[C_7H_{11}]^+$ ions from 2-norbornyl bromide and iodide to be 9.62 and 8.90 eV, respectively, giving $\Delta H_f[C_7H_{11}]^+ = 182.7$ and 182.8 kcal mol^{-1}.[16] In view of the good agreement between these two values there seems to be no doubt that this AE result of 183 kcal mol^{-1} is significantly lower than the (average) 186 kcal mol^{-1} from ion–molecule reactions. We suggest that the AE result corresponds to a $[C_7H_{11}]^+$ ion which has rearranged to a more stable isomer (possibly a tertiary or allylic ion) during the dissociative ionization process. It has been suggested that this rearrangement does not occur under the gentler conditions[9] of the ion–molecule reaction. We have therefore used the 186 kcal mol^{-1} value for our estimate of $D(R^+-H^-)$ for 2-norbornyl cation. In view of the long controversy[17] over the configuration of this ion, it is interesting to see that its $D(R^+-H^-)$ value agrees with recent results that in the gas phase the 2-norbornyl cation has a stability that is closer to that of a tertiary ion than a secondary ion. It lies 10 kcal mol^{-1} below the value it would have as a secondary ion, in good agreement with the recent calculation by Schleyer et al.[18] which gave the "hypothetical classical–non-classical energy difference" for 2-norbornyl ion to be 15 kcal mol^{-1}. The identity of the postulated more stable isomer of $[C_7H_{11}]^+$ formed in the dissociative ionization processes in norbornyl bromide and iodide is currently under investigation in this laboratory.

In Figure 2 the $D(R^+-H^-)$ values from Table III for olefinic and acetylenic ions are plotted against the logarithm of the number of atoms. As mentioned above, some of the $\Delta H_f(R^+)$ values for these were derived from the ionization energy of the radicals rather than from appearance energies because of rearrangements during dissociative ionization. A rearrangement following ionization of a radical has, of course, no effect on the measured IE. In Figure 2, solid circles represent ions which possess allylic π systems which extend over the whole carbon skeleton, that is, the size of the delocalization system corresponds to the ionic size. For these ions, a good straight-line relationship is found. Surprisingly, substituted allylic ions,

$$[C\overset{\cdots}{-}C\overset{\cdots}{-}C]^+$$

and substituted propargyl or allenyl ions,

$$(C\overset{\cdots}{=}C\overset{\cdots}{-}C)^+$$

have the same ionic stabilization within the experimental error (±2 kcal mol^{-1}). A number of ions, shown as hollow or partially filled circles, are those in which the π system does *not* extend over the whole carbon skeleton. These are allylic ions which have been substituted on "unstarred" C atoms, and consequently the effective charge-delocalizing system is smaller than the ionic size. The points therefore are displaced to the right of the line. Furthest of all above the line is the antiaromatic $[C_5H_5]^+$ cyclopentadienyl ion.[19]

The doubly allylic $[C_5H_7]^+$ pentadienyl ion has 10 kcal mol^{-1} more stabilization energy than a singly allylic ion of the same size. At the same level of stabilization is the isomeric cyclopentenyl ion, whose unusual stability has been pointed out earlier.[19b,20] This equality cannot arise from experimental confusion between the two isomers, because the ionic heats of formation differ by 18 kcal mol^{-1}.

In Figure 3 a good straight line is obtained for three members of the family of ions containing $(4n + 2)$ π electrons, i.e., aromatic ions as described by Huckel's rule.[21,22] These are the cyclo-

Table III. Thermochemical Values for Olefinic and Acetylenic Ions (kcal mol^{-1})

structure	$\Delta H_f(R^+)$	ref	$D(R^+-H^-)$
$HC{\equiv}C$	403	52	386
$H_2C{=}CH$	265	25	287
cyclopropenyl	256	28	225
propargyl	281	28	271
allyl	226	27, 28, 29	256
$CH_2{=}CCH_3$	231	53	261
cyclopropyl	234	44	256
$CH_2{=}CCH{=}CH_2$	246	54	254
$CH_3C{\equiv}CCH_2$	252	55	252
$CH{\equiv}CCHCH_3$	257	56	252
methylcyclopropenyl	237	57	212
$CH_2{=}CHCHCH_3$	206	28, 59	241
$CH_2{=}C(CH_3)CH_2$	211	28	250
cyclopentadienyl	255	19b	258
$CH{\equiv}CCHCH{=}CH_2$	271	60	242
$CH_2{=}CHCHCH{=}CH_2$	217	58	226
$CH{\equiv}CC(CH_3)_2$	234	58	236
cyclopentenyl	199	20, 58	226
dimethylcyclopropenyl	217 est.	58, 68	204
$CH_3CH{=}CHCHCH_3$	186	58	228
$CH_3CH{=}CCH_2CH_3$	191	61	233
$CH_2{=}CHC(CH_3)_2$	184	58	225
$CH_3CH{=}C(CH_3)CH_2$	191	62	236
phenyl	267	31	282
c-C_6H_9	191	63	227
trimethylcyclopropenyl	199 est.	58, 68	196
methylcyclopentenyl	190	65	226
$CH_3C{\equiv}CC(CH_3)_2$	216	66	228
benzyl	215	32	238
cycloheptatrienyl	207	67	198

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(13) Solomon, J. J.; Field, F. H. *J. Am. Chem. Soc.* **1976**, *98*, 1567. ($\Delta H_f(t\text{-Bu}^+)$ corrected to 166 kcal mol^{-1}, ref 14.)

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(15) Steele, W. Y. *Chem. Thermodynam.* **1978**, *10*, 919.

(16) Compounds used in this study were the exo halides. From additivity,[2] $\Delta H_f(\text{2-norbornyl bromide}) = -12.4$ kcal mol^{-1}; $\Delta H_f(\text{2-norbornyl iodide}) = +3.1$ kcal mol^{-1}. This calculation corresponds to the more stable forms, i.e., without correction for endo interaction.

(17) For a recent review see a collection of four papers: Grob, A. C. *Acc. Chem. Res.* **1983**, *16*, 426. Brown, H. C. *Ibid*, **1983**, *16*, 432. Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Ibid.* **1983**, *16*, 440. Walling, C. *Ibid.* **1983**, *16*, 448.

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propenyl, methylcyclopropenyl, and cycloheptatrienyl ions. The heat of formation for the methyl cyclopropenyl ion was obtained from the appearance energy for H loss from 1-butyne, AE = 10.85 eV, giving $\Delta H_f[C_4H_5]^+$ = 237 kcal mol^{-1}. This fragment ion is clearly not $[HC{\equiv}CC^+HCH_3]$, for which the heat of formation is 257 kcal mol^{-1} (Table III). In common with the behavior of other propargyl derivatives[23] a rearrangement to give the substituted cyclopropenyl isomer, which is 20 kcal mol^{-1} more stable, has occurred. Values estimated in two ways[58,68] for dimethyl- and trimethylcyclopropenyl ions are identical and are shown in Figure 3 as dotted circles. Their agreement with the experimental line is excellent.

Conclusion

In this report we have shown that $D(R^+{-}H^-)$ used as a direct measure of ion stabilization in a wide range of carbocations can be simply related to ion size, in that $D(R^+{-}H^-)$ is proportional to the logarithm of the number of atoms in the ion.

Registry No. CH_3, 2229-07-4; C_2H_5, 2025-56-1; *n*-C_3H_7, 2143-61-5; *sec*-C_3H_7, 2348-55-2; *t*-C_4H_9, 1605-73-8; C_2H_5CO, 15843-24-0; C_6H_5CO, 2652-65-5; $HC{=}CO$, 51095-15-9; CH_2CN, 2932-82-3; H_2N, 13770-40-6; CH_3NH, 15622-51-2; CH_2NH_2, 10507-29-6; CH_3NHCH_2, 31277-24-4; CH_3CHNH_2, 30208-36-7; CH_3O, 2143-68-2; $HC{\equiv}CCH_2O$, 92056-62-7; C_6H_5O, 2122-46-5; CH_2OH, 2597-43-5; CH_3CHOH, 2348-46-1; $(CH_3)_2COH$, 5131-95-3; *n*-$C_4H_9^+$, 25453-90-1; *n*-$C_5H_{11}^+$, 25453-92-3; *neo*-$C_5H_{11}^+$, 14128-47-3; *n*-$C_6H_{13}^+$, 39749-96-7; c-$C_3H_5^+$, 1724-43-2; *sec*-$C_4H_9^+$, 16548-59-7; c-$C_5H_9^+$, 25076-72-6; *sec*-$C_5H_{11}^+$, 25453-93-4; c-$C_6H_{11}^+$, 22499-63-4; *t*-$C_5H_{11}^+$, 17603-15-5; *t*-$C_6H_{13}^+$, 17603-17-7; *t*-CH_3-c-$C_5H_8^+$, 17106-22-8; *t*-$C_7H_{15}^+$, 19220-62-3; *t*-$C_8H_{17}^+$, 64278-21-3; *t*-$C_9H_{19}^+$, 92056-65-0; $HC{\equiv}C^+$, 16456-59-0; $H_2C{=}CH^+$, 14604-48-9; $CH_2{=}CCH_3^+$, 50457-57-3; $CH_2{=}CCH{=}CH_2^+$, 62698-26-4; $CH_3C{\equiv}CCH_2^+$, 64235-83-2; $CH{\equiv}CCHCH_3^+$, 72183-36-9; $CH_2{=}CHCHCH_3^+$, 17171-50-5; $CH_2{=}C(CH_3)CH_2^+$, 17542-17-5; $CH{\equiv}CCHCH{=}CH_2^+$, 50706-18-8; $CH_2{=}CHCHCH{=}CH_2^+$, 54448-32-7; $CH{\equiv}CC(CH_3)_2^+$, 58175-94-3; $CH_3CH{=}CHCHCH_3^+$, 22537-04-8; $CH_3CH{=}CCH_2CH_3^+$, 92056-66-1; $CH_2{=}CHC(CH_3)_2^+$, 18833-82-4; $CH_3CH{=}C(CH_3)CH_2^+$, 71983-42-1; $CH_3C{\equiv}CC(CH_3)_2^+$, 53474-96-7; 3-cyclohexen-1-ylium, 57127-06-7; allyl radical, 1981-80-2; propargyl radical, 2932-78-7; cyclopentadienyl radical, 2143-53-5; phenyl radical, 2396-01-2; benzyl radical, 2154-56-5; formyl radical, 2597-44-6; acetyl radical, 3170-69-2; methylium, 14531-53-4; ethylium, 14936-94-8; propylium, 19252-52-9; 1-methylethylium, 19252-53-0; 1,1-dimethylethylium, 14804-25-2; 2-propenylium, 1724-44-3; 2-propynylium, 21540-27-2; cyclopentadienylium, 29661-18-5; phenylium, 17333-73-2; phenylmethylium, 6711-19-9; oxomethylium, 17030-74-9; 1-oxoethylium, 15762-07-9; 1-oxopropylium, 17158-30-4; oxophenylmethylium, 19270-10-1; oxoethenylium, 92056-63-8; cyanomethylium, 34430-18-7; aminylium, 15194-15-7; methylaminylium, 49784-84-1; aminomethylium, 54088-53-8; *N*-methylenemethanamine conjugate acid, 51943-18-1; 1-aminoethylium, 82208-60-4; methyloxoniumylidene, 58157-09-8; 2-propynyloxoniumylidene, 92056-64-9; phenyloxoniumylidene, 41071-17-4; formaldehyde conjugate acid, 18682-95-6; acetaldehyde conjugate acid, 18682-96-7; 2-propanone conjugate acid, 43022-03-3; 2-norbornyl cation, 24321-81-1; cyclopropenyl cation, 26810-74-2; methylcyclopropenyl cation, 60824-24-0; cyclopentenyl cation, 18403-29-7; dimethylcyclopropenyl cation, 58419-18-4; trimethylcyclopropenyl cation, 26827-04-3; methylcyclopentenyl cation, 92056-67-2; cycloheptatrienyl cation, 26811-28-9; 2-cyclohexen-1-ylium, 38132-10-4.

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(54) AE for CH_3 loss from isoprene = 11.44 eV; AE for CH_3 loss from 1,4-pentadiene = 11.04 eV.

(55) Ionization energy of radical = 7.95 eV; ΔH_f(radical) = 69 kcal mol^{-1} (ref 24).

(56) Ionization energy of radical = 7.97 eV; ΔH_f(radical) = 73 kcal mol^{-1} (ref 24).

(57) AE for H loss from 1-butyne = 10.85. See text.

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(60) Ionization energy of radical = 7.88 eV. This radical was produced by thermolysis of 4-vinyl-1-hexene 5-yne to give the radical plus allyl radical. Its heat of formation was estimated by assuming that $D(R{-}H)$ was the same as $D(H{-}CH(CH{=}CH_2)_2)$ = 77 kcal mol^{-1} (ref 24). Then from $D(R{-}H)$ = 77 kcal mol^{-1}, and $\Delta H_f(HC{\equiv}CCH_2CH{=}CH_2)$ = 64.1 kcal mol^{-1} by additivity,[2] we obtain ΔH_f(radical) = 89 kcal mol^{-1}.

(61) AE for ethyl loss from 3-ethyl-2-pentene = 10.32 eV.

(62) AE for methyl loss from 3-methyl-2-pentene = 10.42 eV. This is the lower energy process of the two possible.

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(66) AE for methyl loss from 4,4-dimethyl-2-pentyne = 9.72 eV; loss of the acetylenic methyl would be a much more energetic process.

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