with values calculated from reported absolute quantum yields of these compounds (in parentheses in Table I). The value for DPA deviates significantly from that reported. There are several possible causes for this increased triplet yield, and the case is being studied in more detail.[17]

We noted previously that deuteration at outer rings as in perdeuterio-DBA failed to give an enhancement of T_2 lifetime.[3c] The result with PA-d_{10} now shows that deuteration at C_{10} also does not have a significant effect on the T_2 lifetime. There is, however, a definite increase in its intersystem crossing efficiency.

Experimental Section

Fluorescence Quenching. Fluorescence spectra was recorded on a Hitachi Perkin-Elmer MPF-2 spectrometer. Quenching constants were determined from Stern–Volmer plots of relative fluorescence intensities (ϕ_f^0/ϕ_f) *vs.* quencher concentrations. Results of a representative case of the DBA–cyclohexadiene system are shown in Table II.

Quantum Yield Measurements. Degassed samples were prepared in the usual manner[3c] and irradiated in a "merry-go-round" apparatus.[18] Conditions of irradiation and glc conditions for product analysis for each system are shown in Chart I. In the last case in Chart I only relative quantum yields were determined. They are shown in Table III.

Chart I

	Irrad wavelength, Å	Glc conditions for analysis	Actinometer
Cyclohexadiene	3600	10 ft 30% PEG column 130° (monomer) 230° (dimer)	$Ph_2C{=}O$ + *cis*-P
Pentadiene (P)	3600	25 ft 15% TCEP at 40°	$Ph_2C{=}O$ + *cis*-P
endo-Dicyclopentadiene	3800	6 ft 15% FFAP at 190°	None

Table II.[a–c] Fluorescence Quenching of 9,10-Dibromoanthracene by 1,3-Cyclohexadiene (Relative Intensity Units)

[Q], *M*	ϕ_f^0/ϕ_f
0.00	1.00
0.021	1.18
0.031	1.21
0.063	1.22
0.105	1.25
0.262	1.31
0.704	1.36
0.784	1.46
1.060	1.56
1.150	1.66
1.410	1.77

[a] Excitation wavelength, 3600 Å. [b] [DBA] = 1.07 × 10^{-3} *M*. [c] Solvent was benzene.

Table III. Relative Quantum Yields of T_2 Energy Transfer with Dicyclopentadienone[a]

	Product concn,[b] *M*			
[EDP], *M*	DBA	DCA	PA	DPA
0.0363	0.0133	0.0164	0.0171	0.0134
0.0726	0.0336	0.0302	0.0354	0.0295
0.1452	0.0534	0.0582	0.0666	0.0514
0.4356	0.1394	0.1254	0.1537	0.1336
1.163	0.2045	0.1737	0.1864	0.1765

[a] [DBA] = 1.18 × 10^{-3} *M*; [PA] = 9.90 × 10^{-4} *M*; [DCA] = 1.15 × 10^{-3} *M*; [DPA] = 1.24 × 10^{-3} *M*. [b] All samples irradiated for 16.6 days in a M-G-R quantum yield apparatus with Corning 0-51 and 7-60 filter plates.

Acknowledgment. This work was supported by a grant from the National Science Foundation (GP-14248).

---

[17] An interesting but speculative explanation to the cause of increased intersystem crossing in DPA is the existence of the $S_1 \rightleftarrows T_2$ equilibrium. In the absence of triplet acceptors fluorescence, $S_1 \rightarrow S_0$ is the predominant process, and with a high concentration of acceptors transfer from T_2 becomes competitive resulting in a higher "intersystem crossing value."

[18] F. G. Moses, R. S. H. Liu, and B. Monroe, *Mol. Photochem.*, 2, 245 (1969).

Heats of Formation of Free Radicals by Mass Spectrometry

D. K. Sen Sharma and J. L. Franklin*

Contribution from the Department of Chemistry, Rice University,
Houston, Texas 77001. Received May 21, 1973

Abstract: The appearance potentials and translational energies at onset of CH_3^+ from several hydrocarbons and amines have been determined by electron impact in a sector field mass spectrometer. The translational energy was determined by the deflection method and the total excess energy was computed from it. Very good agreement of the heats of formation of ethynyl, propargyl, allyl, amino, methylamino, and dimethylamino radicals with previous determinations was obtained. Reasonable values were also obtained for the dimethyl allyl, dimethyl propargyl, and CH_2NH_2 radicals, but there were no previous values to which ours could be compared. Results for two more complex radicals appear to be somewhat in error, possibly because of the large correction factor resulting from the large number of vibrational modes.

Bond strengths or free radical heats of formation have often been obtained by determining the appearance potential of an ion formed in a known process and independently measuring the ionization potential of the radical. The bond strength is then taken as the difference between the two measurements. Thus

$$R_1R_2 + e \longrightarrow R_1^+ + R_2 + 2e \quad - AP(R_1^+)$$

$$R_1 + e \longrightarrow R_1^+ + 2e \quad - IP(R_1)$$

$$AP(R_1^+) - IP(R_1) = D(R_1\text{–}R_2)$$

This is an excellent method but suffers from two disadvantages: (1) it requires special equipment and often quite difficult techniques to generate the free radical whose ionization potential is to be determined; (2) the appearance potential of R_1^+ may involve excess energy which will cause serious errors if not corrected for.

An alternative procedure would be to determine the appearance potential of R_2^+ in the reaction

$$R_1R_2 + e \longrightarrow R_1 + R_2^+ + 2e - AP(R_2^+)$$

If $\Delta H_f(R_2^+)$ and $\Delta H_f(R_1R_2)$ are known, $D(R_1\text{–}R_2)$ can also be calculated. Of course, the appearance potential of R_2^+ may involve excess energy which must be corrected for.

This investigation was undertaken to demonstrate the applicability of this approach to the measurement of the heats of formation of free radicals and ions. For this purpose we selected certain hydrocarbon free radicals and ions, the majority of which have been extensively studied, and several alkyl amines, which have been relatively little studied but whose bond strengths could at least be estimated with some confidence. The hydrocarbon radicals were allyl, propargyl ethynyl, dimethyl allyl, and dimethyl propargyl. The nitrogen-containing radicals were NH_2, CH_3NH, $(CH_3)_2N$, CH_2NH_2, $CH_2N(C_2H_5)H$, and $CH_2N(C_2H_5)_2$. The heats of formation of each of these radicals were determined by measuring the appearance potentials of CH_3^+ in the process

$$CH_3R + e \longrightarrow CH_3^+ + R + 2e$$

The heats of formation of $C_3H_5^+$, $C_3H_3^+$, and NH_2^+ were also determined by measuring the appearance potential of the ion in the process

$$RCH_3 + e \longrightarrow R^+ + CH_3 + 2e$$

In all cases it was necessary to determine the excess energy at or very near the appearance potential. This was done by measuring the translational energy, $\bar{\epsilon}_i$, of the ion and computing the total translational energy in the center of mass, $\bar{\epsilon}_t$, from the relation

$$\bar{\epsilon}_i = (m_i/m)(^3/_2kT) + (m_n/m)\bar{\epsilon}_t$$

where m_i and m_n are the masses of the ion and neutral fragments, respectively, and $m = m_i + m_n$. Haney and Franklin[1] have shown from empirical comparisons of $\bar{\epsilon}_t$ and total excess energy, E^*, of several processes that the RRK treatment with an added empirical constant gives an excellent correlation of $\bar{\epsilon}_t$ and E^*, the final equation being

$$\bar{\epsilon}_t = E^*/\alpha N$$

where N is the number of vibrational modes and α is an empirical constant that Haney and Franklin[1] found to be 0.44. Thus the appearance potential and the translational energy of each ion were determined and the heat of formation of the radical or ion of interest was calculated from these results.

Experimental Section

The mass spectrometer employed in these studies is a 12-in. radius 60° sector field, electron impact instrument equipped with a 14-stage multiplier and vibrating reed electrometer for signal enhancement. A conventional source and ion gun were employed for measuring appearance potentials. Translational energies were measured by the deflection method of Taubert.[2] For this a shortened ion gun was employed and a variable electric field applied across deflection plates mounted just inside the analyzer to sweep the ion beam across the collector slit. The instrument and method have been described in detail elsewhere.[3]

$\bar{\epsilon}_i$ was obtained from the deflection data by graphical integration. It can be shown that

$$\bar{\epsilon}_i = \mu_d^2/K^2$$

where μ_d is the potential across the deflection plates and K is a constant obtained by a standard calibration procedure. A plot of $\bar{\epsilon}_i$ against relative intensity can be integrated graphically and the average ion energy, $\bar{\epsilon}_i$, obtained. A simpler procedure would be to compute the average energy from the peak width at half-height. This is valid if the function is Gaussian, as is true for thermal ions, but gives results that are as much as 30% too low if the distribution function is not Gaussian.[4,5]

Appearance potentials were determined from the ionization efficiency curves in most cases by the extrapolated voltage difference method of Warren[6] together with the vanishing current method as a means of comparison. The ionization efficiency curve of N_2^+ or Ar_2^+ was employed to calibrate the voltage scale. In no cases was it possible to employ semilog plots because the resulting curves were not parallel.

The chemicals used in this study were commercial products obtained from Matheson Co., Inc., and from Matheson Coleman and Bell. Most of these compounds were 96–99% pure. Their stated purities were checked by running their mass spectra.

Results and Discussion

Table I presents the measurements of translational energy of the ions from the various processes. These were determined by graphical integration and, for comparison, from the peak width at half-maximum. As was predicted by Weinstein[4] and as we had found with other ion fragmentation processes,[5] the assumption of a Gaussian distribution which is inherent in the latter method results in average energies that are as much as 50% below the true value. Consequently, in computing the excess energy, E^*, we have in all cases employed the translational energies calculated by graphical integration.

Table I. Average Total Translational Energies and Excess Energies (kcal/mol)

No.	Process	$\bar{E}_t$ KT	$\bar{E}_t$ GI	E^* GI	% deviation
1	$CH_3C{\equiv}CH \rightarrow CH_3^+ + C_2H$	3.3	3.6	23	8
2	$CH_3CH_2CH{=}CH_2 \rightarrow CH_3^+ + C_3H_5$	1.0	2.0	26	50
3	$(CH_3)_3CCH{=}CH_2 \rightarrow CH_3^+ + C_5H_9$	2.2	2.9	61	24
4	$CH_3CH_2C{\equiv}CH \rightarrow CH_3^+ + C_3H_3$	4.0	4.4	46	9
5	$(CH_3)_3CC{\equiv}CH \rightarrow CH_3^+ + C_5H_7$	2.2	2.5	46	12
6	$(CH_3)_2C{=}CH_2 \rightarrow CH_3^+ + C_3H_5$	3.7	4.6	61	20
7	$(CH_3)_2C{=}CH_2 \rightarrow C_3H_5^+ + CH_3$	0.7	1.6	21	56
8	$CH_3CH_2CH{=}CH_2 \rightarrow C_3H_5^+ + CH_3$	1.2	1.2	16	0
9	$CH_3CH_2C{\equiv}CH \rightarrow C_3H_3^+ + CH_3$		1.3	14	
10	$(CH_3)_2NH \rightarrow CH_3^+ + CH_3NH$	2.0	3.1	33	35
11	$(CH_3)_3N \rightarrow CH_3^+ + (CH_3)_2N$	2.5	2.6	38	4
12	$C_2H_5NH_2 \rightarrow CH_3^+ + CH_2NH_2$	3.2	4.4	46	27
13	$(C_2H_5)_2NH \rightarrow CH_3^+ + C_2H_5N(CH_2)N$	1.4	2.0	37	30
14	$(C_2H_5)_3N \rightarrow CH_3^+ + (C_2H_5)_2NCH_2$	2.5	3.0	79	17

---

[1] M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, 48, 4093 (1968).

[2] R. Taubert, *Z. Naturforsch.*, 199, 484 (1963); R. Taubert, *Advan. Mass Spectrom.*, 1, 489 (1959); J. Bracher, H. Ehrhardt, R. Fuchs, O. Osberghaus, and R. Taubert, *ibid.*, 2, 285 (1963).

[3] D. K. Sen Sharma and J. L. Franklin, *Int. J. Mass Spectrom. Ion Phys.*, submitted for publication.

[4] N. Weinstein, *J. Chem. Phys.*, 58, 408 (1973).

[5] J. L. Franklin and D. K. Sen Sharma, *J. Chem. Phys.*, 58, 409 (1973).

[6] J. W. Warren, *Nature (London)*, 165, 810 (1950).

Table II. Appearance Potentials of Ions and ΔH_f of Hydrocarbon Free Radicals and Ions (kcal/mol)

Process	AP This work	AP Lit	E^*	ΔH_0	ΔH_f(R) or (R$^+$) This work	ΔH_f(R) or (R$^+$) Lit
$CH_3C_2H \rightarrow CH_3^+ + C_2H$	369	355[a]	23	346	130	112,[a] 130,[b] 114,[c] 116[d]
$1\text{-}C_4H_8 \rightarrow CH_3^+ + C_3H_5$	326		26	300	40	40,[e,f] 38,[g] 39.6 ± 1.5[h]
$(CH_3)_3CCH{=}CH_2 \rightarrow CH_3^+ + C_5H_9$	354		61	293	19	
$C_2H_5C{\equiv}CH \rightarrow CH_3^+ + C_3H_3$	348		46	302	82	75,[h] 80.7[i]
$(CH_3)_3CC{\equiv}CH \rightarrow CH_3^+ + C_5H_7$	340		46	294	59	
$(CH_3)_2C{=}CH_2 \rightarrow CH_3^+ + C_3H_5$	378		61	317	53	58[j]
$1\text{-}C_4H_8 \rightarrow C_3H_5^+ + CH_3$	271	270,[j] 260,[k] 263[l]	16	255	222[m]	216,[j] 226[k]
$(CH_3)_2C{=}CH_2 \rightarrow C_3H_5^+ + CH_3$	272	264,[k] 272[l]	21	251	214[m]	216,[j] 226[k]
$C_2H_5C{\equiv}CH \rightarrow C_3H_3^+ + CH_3$	270	250,[k] 249,[j] 254[j]	14	256	263[m]	255,[j] 256[k]

[a] Reference 8. [b] Reference 11. [c] Reference 9. [d] Reference 10. [e] Reference 13. [f] Reference 14. [g] Reference 17. [h] Reference 18. [i] Reference 19. [j] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS-26, National Bureau of Standards Reference Data System, U. S. Department of Commerce, 1969. [k] Reference 21. [l] G. G. Meisels, J. Y. Park, and B. G. Geissner, *J. Amer. Chem. Soc.*, **91**, 1555 (1969); **92**, 254 (1970). [m] ΔH_f(ion).

Table III. Bond Strengths and Stabilization Energies (kcal/mol) from the Experimental Heats of Formation of Free Radicals in Table II

	Bond strength	Stabilization energy		Bond strength	Stabilization energy
$D(n\text{-}C_3H_7\text{–}H)$	98		$D[(CH_3)_3C\text{–}H]$	91	
$D(C_2H_3CH_2\text{–}H)$	88	10	$D[C_2H_3(CH_3)_2C\text{–}H]$	78	13
$D(HC_2CH_2\text{–}H)$	90	8	$D[HC_2(CH_3)_2C\text{–}H]$	79	12

Table IV. Appearance Potentials of Ions and Heats of Formation of Free Radicals from Amines (kcal/mol)

Process	AP This work	AP Lit	E^*	ΔH_0	ΔH_f(R) This work	ΔH_f(R) Lit
$CH_3NH_2 \rightarrow CH_3^+ + NH_2$	334	339[a]	27	307	41	41,[b] 43.3 ± 3,[c] 40,[d] 47 ± 2[i]
$CH_3NH_2 \rightarrow CH_3 + NH_2^+$	367	360[a]	24	343	304[e]	304[f]
$(CH_3)_2NH \rightarrow CH_3^+ + CH_3NH$	341		33	308	43.6	37,[g] 34.3 ± 2,[d] 41.7,[c] 45 ± 2[i]
$(CH_3)_3N \rightarrow CH_3^+ + (CH_3)_2N$	343		38	305	39	34,[g] 29.3 ± 2,[d] 37.4,[c] 38 ± 2[i]
$C_2H_5NH_2 \rightarrow CH_3^+ + CH_2NH_2$	360		46	314	43	37[h]
$(C_2H_5)_2NH \rightarrow CH_3^+ + CH_2N(C_2H_5)H$	355		37	318	37	32[h]
$(C_2H_5)_3N \rightarrow CH_3^+ + CH_2N(C_2H_5)_2$	386		79	307	21	23[h]

[a] Reference 1. [b] Footnote *j* of Table II. [c] Reference 17. [d] Reference 14. [e] ΔH_f(ion). [f] Reference 8. [g] B. G. Gowenlock, P. P. Jones, and J. R. Majer, *Trans. Faraday Soc.*, **57**, 23 (1961). [h] Reference 23. [i] Reference 22.

Tables II and III give the appearance potentials of the various processes, E^*, and the heat of the dissociation reaction, ΔH_0, determined as the difference between them. From these and the known thermochemical data given in Table VI, the heats of formation of the radicals and ions of interest are calculated. The results are given in the tables along with results of other investigators for comparison.

Ethynyl Radical. Values for $\Delta H_f(C_2H)$ have varied more widely over the years than have those of almost any other radical. Steacie and Leroy,[7] using photochemical data, found $\Delta H_f(C_2H)$ to be less than 110 kcal/mol, and Coats and Anderson,[8] using an electron impact method, found values from 110 to 150 kcal/mol but preferred 112 kcal/mol as the most probable value. The most recent JANAF tables[9] quote a preferred value of 114 and Tsang, *et al.*,[10] found 116 kcal/mol. More recently Wyatt and Stafford[11] employing high temperature mass spectrometry found $\Delta H_f(C_2H)$ to be 130 kcal/mol in exact agreement with our value. Naturally we think the higher is the more nearly correct. The methods we employed should, if anything, give low rather than high values. The work of Wyatt and Stafford[11] should be quite accurate and it is difficult to see how either method could be in error by more than a very few kilocalories per mole. Thus, we think it would be very surprising if $\Delta H_f(C_2H)$ were as low as 125 kcal/mol and we think 130 kcal/mol to be the probable value.

Allyl Radical. An early determination by McDowell, *et al.*,[12] gave ΔH_f(allyl) to be 32 ± 6 kcal/mol. The resonance energy of benzene, taken as the difference between the heats of hydrogenation of benzene and of three *cis*-2-butenes, is about 38 kcal/mol and that of allyl radical is 19 kcal/mol if the value of McDowell, *et al.*,[12] is correct. Since native molecular orbital theory predicts the resonance energy of allyl to be one-half that of benzene, the value of McDowell, *et al.*,[12] seemed correct.

Recent investigations, however, all give higher values

---

(7) E. W. R. Steacie and D. J. Leroy, *J. Chem. Phys.*, **12**, 117 (1944).

(8) F. H. Coats and R. C. Anderson, *J. Amer. Chem. Soc.*, **79**, 1340 (1957).

(9) "JANAF Thermodynamic Tables," D. R. Stull, Ed., Clearing House for Federal Scientific and Technical Information, Springfield, Va., 1968, Document no. PB-168, tables as issued to Jan 1971, p 370.

(10) W. Tsang, S. H. Bauer, and M. Cowperthwaite, *J. Chem. Phys.*, **36**, 1768 (1962).

(11) J. R. Wyatt and F. E. Stafford, *J. Phys. Chem.*, **76**, 1913 (1972).

(12) C. A. McDowell, F. P. Lossing, I. H. S. Henderson, and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1966).

for $\Delta H_f(C_3H_5)$ than 32 kcal/mol. Lossing,[13] employing a monochromatic electron beam, determined the appearance potential of $C_3H_5^+$ from several compounds and from the allyl radical. From these he deduced a value of 40 kcal/mol for ΔH_f(allyl). Kerr[14] calculated ΔH_f(allyl) to be 38 ± 1 kcal/mol from bond dissociation data. Studies by Benson and his group employing careful kinetic methods gave values of 40.6[15] and 38[16] kcal/mol, and Benson and O'Neal[17] concluded that 39.6 ± 1.5 kcal/mol was the preferred value of ΔH_f(allyl). Our value is thus in accord with the recent high values of ΔH_f(allyl) and agrees reasonably well with Benson and O'Neal's[17] preferred value. We thus conclude that the earlier values of ΔH_f(allyl) were erroneously low and that the probable value is very near 40 kcal/mol.

We thought it of interest to determine the heat of formation of the $CH_3C{=}CH_2$ radical, which we did by measuring the appearance potential and translational energy of CH_3^+ from isobutene. Our value of 53 kcal/mol would yield a D(R–H) in propene of 100 kcal/mol. This is about 5 kcal/mol less then $D(C_2H_3{-}H)$, as would be expected. It is somewhat surprising that the C_3H_5 radicals from 1-butene and isobutene appear to be different as judged by the substantial differences in their heats of formation. Unfortunately there are no similar measurements to which these may be compared. It appears from the large difference in AP(CH_3^+) between the two butenes that different electronic states may be involved. It is possible that we may have made an error in either our appearance potential or translational energy measurements. If the appearance potential of CH_3^+ from isobutene were 0.5 V too high or if the translational energy were 1 kcal/mol too low, the calculated $\Delta H_f(C_3H_5)$ would be about the same as allyl. We do not think our measurements are that much in error, however, and so we conclude that the difference is real and that the radical from isobutene is probably isoallyl.

Propargyl Radical. From early electron impact studies, Collin and Lossing[18] deduced $\Delta H_f(C_3H_3)$ to be 75 kcal/mol. A recent shock tube study of 4-methyl-1-pentyne by Tsang[19] yielded a $\Delta H_f(C_3H_3)$ of 80.7 kcal/mol. Walsh,[20] studying the kinetics of the iodine-catalyzed isomerization of propyne, found $\Delta H_f(C_3H_3)$ to be 86 kcal/mol. Our value falls in the midst of these previously determined ones and is quite close to that of Tsang.[19]

Dimethyl Allyl and Dimethyl Propargyl Radicals. The dimethyl allyl (C_5H_9) and dimethyl propargyl (C_5H_7) radicals have not been studied before. The values we have determined appear reasonable, however. If we compute the stabilization or electron delocalization energies of the two allyl and propargyl radicals, we find fairly close agreement. This was done by comparing D(R–H) of propene and propyne with that of the primary C–H bond of propane and of the methyl substituted radicals with the tertiary C–H bond in isobutane. The results are given in Table III and show fairly good agreement. Although there is a 5-kcal/mol spread in the values, the maximum deviation from the mean is less than 3 kcal/mol and is within the accuracy of the data. The results are thus consistent, as they should be, and since our allyl and propargyl values are in excellent agreement with the best values obtained by others, it seems reasonable that the heats of formation of the methyl substituted radicals are also correct.

$C_3H_5^+$ and $C_3H_3^+$. Lossing[21] has recently surveyed the appearance potentials of $C_3H_5^+$ and $C_3H_3^+$ ions. In addition, he has determined the appearance potentials from several compounds employing an energy selected electron beam for his measurements. His values for $\Delta H_f(C_3H_3^+)$ and those of several other investigators are within about 2 kcal/mol of 257. The ionization potential of propargyl is 8.68 eV and this, combined with our $\Delta H_f(C_3H_3)$, gives the heat of formation of propargyl ion to be 282 kcal/mol. The $C_3H_3^+$ ion whose heat of formation is 257 kcal/mol is thus some 25 kcal/mol more stable than the propargyl ion. Lossing concluded that this more stable ion is probably cyclic, in accordance with the rule that aromatic stability is achieved for cyclic structures having $4n + 2$ ring π electrons. Our value, $\Delta H_f(C_3H_3^+) = 263$ kcal/mol, is too small for the ion to be propargyl and so we conclude that the ion was the cyclic $C_3H_3^+$ and that our determination gave results that are about 6 or 7 kcal/mol too high. Comparing our measurements with those of other workers suggests that our appearance potential was somewhat too high.

Lossing's[21] determination of $\Delta H_f(C_3H_5^+)$ from several compounds gave all of the values in the range 225–227 kcal/mol, in very close agreement with the 226 kcal/mol that he obtained from his ionization potential of allyl radical of 8.07 eV combined with the heat of formation of the radical. Our determination of $\Delta H_f(C_3H_5^+)$ from 1-butene is in fair agreement with Lossing's value. Further, our heat of formation of the radical combined with its ionization potential gives $\Delta H_f(C_3H_5^+)$ to be 227 kcal/mol in close agreement with Lossing's. We also determined $\Delta H_f(C_3H_5^+)$ from isobutene. Our value is only 214 kcal/mol and is thus considerably below Lossing's value and our value from 1-butene. We are at a loss to understand the discrepancy. It appears that our measurement over corrected for excess energy, but if so, this is quite unusual since we find the method to be quite reliable in all other instances.

Amino and Amine Substituted Methyl Radicals. Table IV presents our determinations of the heats of formation of NH_2, CH_3NH, and $(CH_3)_2N$ radicals. The results for the latter two agree within 2 kcal/mol with those recommended by Benson and O'Neal[17] and the more recent ones determined by Golden, *et al.*,[22] and thus appear to be satisfactory. The CH_3–R bond dissociation energies computed from our ΔH_f(R) are in the expected range.. However, our value for $\Delta H_f(NH_2)$ is much smaller than that of Golden, *et al.*,[22] but agrees closely with the slightly older value recom-

---

[13] F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971).

[14] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[15] A. S. Rogers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966).

[16] E. K. Eggers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964).

[17] S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS-21, National Bureau of Standards Reference Data System, U. S. Department of Commerce, 1970.

[18] J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **79**, 5848 (1957).

[19] W. Tsang, *Int. J. Chem. Kinet.*, **2**, 23 (1970).

[20] R. Walsh, *Trans. Faraday Soc.*, **62**, 2085 (1971).

[21] F. P. Lossing, *Can. J. Chem.*, **50**, 3973 (1972).

[22] D. M. Golden, R. K. Sally, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 363 (1972).

mended by Benson and O'Neal. It would be expected that the heats of formation of these radicals would decrease somewhat with each replacement of H by CH_3. It thus appears that the older value of NH_2 and our own is too low or the new value of $\Delta H_f(CH_3NH)$ and ours is too high. Although a definite conclusion cannot be reached, we are inclined to think the older values of $\Delta H_f(NH_2)$ are too small. If this is true we are at a loss to understand why our value is too low, but we are inclined to think our appearance potential may be erroneously low. If our value of E^* is combined with Haney and Franklin's[1] appearance potential, $\Delta H_f(NH_2)$ becomes 46 kcal/mol in good agreement with the value of Golden, *et al.*[22]

The strength of the C–N bonds in the methylamines is given in Table V; these also agree reasonably and are of about the expected magnitude. The heats of formation of the three free radicals formed by breaking a C–C bond in each of the three ethylamines are also given in Table IV. There are no previous measurements of the heats of formation of these radicals with which to compare our results. They are compared with the corresponding heats of formation computed by the method of group equivalents.[23] The agreement is not good but the group equivalent values are dependent upon the heats of formation of the amines employed to compute the group equivalents and with the amines these are not consistent within the group. If we examine the strengths of the C–C bonds in Table V, the variation is not the one expected. Although it is not possible to determine definitely whether our values are in error, it seems likely that for $CH_2(C_2H_5)NH$ is several kilocalories per mole too high and that of $CH_2(C_2H_5)_2N$ perhaps slightly too low. The large number of vibrational modes (42 and 60) in these molecules multiplies any error in the determinations of the translational energy by a large factor so that the correction for excess energy may be considerably in error. Thus, although our measurement of translational energy is quite precise, the correction factor may still be quite large for molecules with a sufficient number of vibrational modes. Thus αN for $(C_2H_5)_2NH$ and $(C_2H_5)_3N$ are 18.5 and 26.4, respectively, so that an error in $\bar{\epsilon}_t$ of 200 small calories would cause an error of 3.7 and 5.2 kcal/mol, respectively. An error of 100–300 calories in $\bar{\epsilon}_t$ is not unreasonable and thus an error of 3–5 kcal/mol in E^* might be expected for molecules of this complexity. This could well account for the apparent discrepancies among the three C–C bonds in Table V.

Table V. Bond Strengths (kcal/mol) Calculated from Heats of Formation of Free Radicals in Table IV

	D(C–N)	D(C–C)
$CH_3NH_2 \rightarrow CH_3 + NH_2$	79.5	
$(CH_3)_2NH \rightarrow CH_3NH + CH_3$	81	
$(CH_3)_3N \rightarrow (CH_3)_2N + CH_3$	78	
$C_2H_5NH_2 \rightarrow CH_3 + CH_2NH_2$		87.3
$(C_2H_5)_2NH \rightarrow CH_3 + (C_2H_5)(H)NCH_2$		91
$(C_2H_5)_3N \rightarrow CH_3 + (C_2H_5)_2NCH_2$		80

Table VI. Heats of Formation of Ions and Neutrals (kcal/mol)[a]

Species	$\Delta H_f°$	Species	$\Delta H_f°$
CH_3^+	260	$(C_2H_5)_3N$	−26.0
CH_3	33, 34.0 ± 0.5[b]	$CH_3C{\equiv}CH$	44.3
n-C_3H_7	21[c]	$CH_3CH_2CH{=}CH_2$	−0.03
t-C_4H_9	6.8[c]	$(CH_3)_3CCH{=}CH_2$	−14.3
CH_3NH_2	−5.5	$CH_3CH_2C{\equiv}CH$	−39.5
$(CH_3)_2NH$	−4.4	$(CH_3)_3CC{\equiv}CH$	25.0[d]
$(CH_3)_3N$	−5.8	$(CH_3)_2C{=}CH_2$	−4.0
$C_2H_5NH_2$	−11.3, −12.2[d]	3-Methyl-1-butene	−6.92[e]
$(C_2H_5)_2NH$	−21.4, −18.0[d]	3-Methyl-1-butyne	32[d]

[a] Taken from foonote *j* of Table II. [b] Taken from S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [c] Taken from F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). [d] Calculated by Franklin's method of group equivalents given in ref 23. [e] Taken from F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Brown, and G. C. Pimentel, "Selected Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Pittsburgh, Pa., 1953.

Acknowledgment. The authors wish to express their appreciation to The Robert A. Welch Foundation for the financial support of this work.

---

(23) Calculated by Franklin's group equivalents method: J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949); *J. Chem. Phys.*, 21, 2029 (1953); or see ref 16.