Excess Energies in Mass Spectra of some Oxygen-containing Organic Compounds

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Excess energies of the electron-impact induced dissociation of several oxygen-containing compounds have been estimated by measuring the translational energies of the fragment ions. The heats of formation of CH_3O, C_2H_5O, CH_3CO, HCO, $COOH$, and their positive ions have been determined. The formyl radical has a heat of formation of 8 ± 3 kcal/mole. Ions of composition CH_3O^+ and $C_2H_5O^+$ from these compounds always have the hydroxy carbinyl structure at threshold energies. The method is shown to be competitive with the best methods of chemical kinetics for determining bond dissociation energies.

Considerable data on the appearance potentials of fragment ions in the mass spectrometer have accumulated.[1] For electron impact, the general process can be represented by

$$R_1R_2 + e^- \rightarrow R_1^+ + R_2 + 2e^-. \tag{1}$$
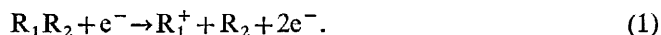
For simple bond-breaking processes R_2 is a radical and R_1^+ is thus an ionized radical. The determination of the heats of formation of these dissociation products is essential to the understanding of most gaseous ionic phenomena. For example, such data are useful for elucidating the mechanisms of both unimolecular and bimolecular reactions occurring in the mass spectrometer. Also, important information can be derived from these heats of formation; i.e., the ionization potential of the R_1 radical and the bond energies in both the neutral and ionized molecule.

The heats of formation of the lower hydrocarbon radicals and ions have been reliably determined by a combination of kinetic and both direct and indirect mass spectrometric methods. Next to the hydrocarbons, the ions and radicals of C,H,O composition are probably of greatest interest because of their widespread occurrence in flames and in the mass spectra of oxygen-containing organic compounds. The purpose of this work is to determine the heats of formation of several radicals and their positive ions which contain only carbon, hydrogen, and oxygen.

By measuring the appearance potential of R_1^+ from reaction (1), the heat of formation of either R_1^+ or R_2 can be calculated (if the heats of formation of the other species are known) by the relation:

$$\text{A.P.} = \Delta H_f(R_1^+) + \Delta H_f(R_2) - \Delta H_f(R_1R_2) + E^*. \tag{2}$$

E^*, the excess energy, is the excitation energy of $R_1R_2^+$ above that necessary to form the products in their ground states. It can arise from a Franck-Condon transition to a point on the potential energy curve above the decomposition asymptote, from an activation energy for the decomposition of the molecular ion, or from the kinetic shift effect.[3] It has usually been neglected for lack of a method to determine it. Recently the authors[2] have shown that this excess energy is partitioned in a statistical

manner among the degrees of freedom of the decomposing molecular ion. In fact, the excess energy was found to be proportional to the number N of internal degrees of freedom and to the average relative translational energy $\bar{\varepsilon}_t$ of the fragments:

$$E^* = 0.44 \, N\bar{\varepsilon}_t \tag{3}$$

The constant of proportionality was found experimentally by measuring the translational energies produced in several reactions with known excess energies. This is the translational energy at the appearance potential of the fragment ion. $\bar{\varepsilon}_t$ can be obtained from the average translational energy of the fragment ion in the laboratory coordinate system, $\bar{\varepsilon}_{R_1^+}$, by conservation of the momentum:

$$\varepsilon_t = \frac{M_{R_1R_2}}{M_{R_2}}\bar{\varepsilon}_{R_1^+} - \frac{M_{R_1^+}}{M_{R_2}}(\tfrac{3}{2}kt). \tag{4}$$

For large molecules, with a correspondingly large number of oscillators, the translational energy is too small a fraction of the excess energy to be measured with accuracy. We are thus confined to molecules of about 10-12 atoms, or less. Also, it would not be prudent to extend eqn. (3) to larger molecules since they were not studied in the earlier work, Another limitation is apparent from eqn. (4). If R_2 is a species of small mass, such as H or H_2, the fragment ion will not possess enough translational energy to measure accurately. These conditions are not as restrictive as they might seem. Indeed, a major goal of this study is to demonstrate the utility of excess energy measurements in energetic studies of ionic dissociations.

EXPERIMENTAL

The methyl ethyl ether was synthesized by Williamson's method and fractionated, b.p. 8-9°C. Methyl and ethyl nitrites were made by dripping a stoichiometric mixture of the alcohol and diluted H_2SO_4 into a cold solution of sodium nitrite. The escaping gas was passed through a solution of sodium hydroxide to remove nitrogen oxides and through a tube of calcium chloride for drying. The ethyl nitrite was distilled, collecting the fraction at 17-18°C, but the methyl nitrite was not. No impurities could be detected mass spectrometrically but the most undesirable impurities expected would be masked by the fragment ions. The appearance potentials of these fragment ions should reveal any interfering impurities. The dimethyl ether was from Matheson. All other chemicals were common reagent grade and used without further purification.

The appearance potentials were determined by the retarding potential difference method on a Bendix model 12 time of-flight mass spectrometer. Either krypton or acetylene was used as the electron energy calibrant. The replicate appearance potentials were run on different days to help eliminate systematic errors.

Translational energy measurements were made on the Bendix instrument in the manner previously described.[2, 4] In general, measurements of translational energy were taken at appropriate intervals ($\tfrac{1}{2}$-2 V) of electron energy and the resulting curve extrapolated to the appearance potential to obtain $\bar{\varepsilon}_{R_1^+}$.

RESULTS AND DISCUSSION

A summary of the data is presented in table 1. Many of these appearance potentials have been measured before by other workers. The " best " value is usually the average of all determinations, including our own. In cases where other data are in serious disagreement with ours, they have been discarded for the sake of consistency.

The maximum expected error for translational energy measurements ($\bar{\varepsilon}_{R_1^+}$) is 0.2 kcal. However, in some cases the extrapolation to the onset for ionization results in an additional uncertainty, as in fig. 1. Also, the error in $\bar{\varepsilon}_t$ depends upon

the mass of R_1^+ relative to R_2 and, to a certain extent, upon the translational energy of R_1^+. The limits of uncertainty placed on $\bar{\varepsilon}_t$ and E^* take all this into consideration. In the previous work, eqn. (3) had an average error of 12 %, including the experimental errors listed above. Consequently, the error listed for E^* in table 1 is taken to be equal to 12 % or to the % uncertainty in $\bar{\varepsilon}_t$, whichever is larger.

The thermochemical data used in this study are presented in table 3. In several cases we have used values for the heat of formation of an ion established independently in this work in order to determine the heat of formation of a radical. These ions are also noted in table 3. Experimental values of the appearance potentials and excess energies are combined with the given thermochemical data to obtain the heats of formation listed in columns 8 and 9 of table 1.

HCO^+

The heat of formation of this ion has a special importance because of the chemi-ionization reaction producing it in flames[5].

$$O + CH \rightarrow HCO^+ + e^- \qquad (5)$$
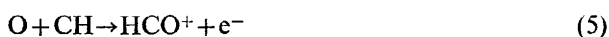
The appearance potential of HCO^+ from aldehydes has led to the value of 222 kcal/mole.[1, 6] Pritchard and Harrison[7] re-examined these appearance potentials and found a best value of 207 ± 3 kcal/mole. Both of these values require the CH radical to have excitation energy if reaction (5) is to proceed rapidly. From formic acid, acetaldehyde, and acrolein, we find an average value of $\Delta H_f(HCO^+) = 198 \pm 2$ kcal/mole. This permits reaction (5) to be slightly exothermic and thus will be expected to proceed at a high rate.

CH_3O^+

Two studies[8, 9] of appearance potentials of this ion have both provided evidence for two distinct structures. The lower energy ion obtained from alcohols and presumed to have the hydroxy carbinyl structure CH_2OH^+ had a heat of formation of ~ 175 kcal/mole. Appearance potentials indicated that the mass 31 ion from ethers and esters had a much higher heat of formation (> 200 kcal/mole). This ion was therefore presumed to have the methoxyl structure H_3CO^+. Our data on dimethyl ether, methyl formate and methyl nitrite indicate that the difference can be attributed to excess energy and the ion formed at the appearance potential is always the CH_2OH^+ ion. If the methoxy ion exists, and is stable, its energy will have to be determined by direct ionization of the CH_3O radical. Its heat of formation must be less than 198 kcal/mole or else it will probably decompose to the formyl ion.

It can be seen from table 1 that there is a discrepancy of about 0·3 eV in the appearance potentials of CH_2OH^+ from ethanol from various workers. Our own value of $11·65 \pm 0·02$ by RPD checks well with that of 11·6 eV by Harrison et al.,[9] and Friedman et al.[10] However, Munson and Franklin[8] and Cummings and Bleakney[11] both report 11·3 eV. In addition, Rafaey and Chupka[12] found 11·25 eV by photo-ionization. If the higher values are taken, we find $\Delta H_f(CH_2OH^+) = 170 \pm 5$ kcal/mole after subtracting for the small and uncertain excess energy. The photo-ionization value apparently does not contain this excess energy and is undoubtedly more accurate. If we take the Rafaey and Chupka appearance potential, we get $\Delta H_f(CH_2OH^+) = 170$ kcal/mole.

The mass 31 ion from methyl ether is probably formed with the products C_2H_4 and H instead of C_2H_5 since the heat of formation comes out much too high if C_2H_5 is assumed. Isotope labelling studies[9] have also suggested that $C_2H_4 + H$ are the neutral products of decomposition.

TABLE 1

process	appearance potential (eV)			ε̄_R₁⁺	ē_t	E* (kcal/mole)	ΔH_f(R₁⁺)	ΔH_f(R₂)
	literature	this work	best value					
HCOOH→HCO⁺+OH	{13·19 ʲ / 12·63 ⁱ 12·70 ᵏ / 12·88 ᵃ	13·03±·01	13·11	**HCO⁺** 1·0±·2	1·1±·5	4±2	199±2	
CH₃CHO→HCO⁺+CH₃	13·99 ᵃ	12·73±·04	12·73	1·8±·2	3·5±·6	23±4	197±4	
C₂H₅CHO→HCO⁺+C₂H₅		13·30±·10	13·30	1·9±·2	3·0±·4	23±3	196±3	
C₂H₅OH→CH₂OH⁺+CH₃	{11·6 ⁱ / 11·3 ᵐ / 11·3 ⁿ	11·6 ᵖ 11·25 q	11·65±·02	11·62 (see text)	**CH₃O⁺** 0·9±·2	0·9±·6	8±5	170±5	
CH₃OCH₃→CH₃O⁺+CH₃	{12·1 ᵐ 12·3 ⁱ / 12·6 ᵇ 12·5 ʳ	11·95±·05 / 12·50	12·29 / 12·7	2·1±·3 / 1·3±·2	4·6±·6 / 1·7±·4	42±6 / 22±5	164±6 / 194±3	
CH₃OC₂H₅→CH₃O⁺+C₂H₅	12·9 ⁱ		(see text)				(see text)	
CH₃ONO→CH₃O⁺+NO	11·0 ᵐ	10·96	10·98	3·4±·2	6·1±·4	40±5	177±5	
2-C₃H₇OH→C₂H₄OH⁺+CH₃ / CH₃OC₂H₅→C₂H₅O⁺+CH₃	{10·9 ᵖ 10·5 ⁱ / 10·40 q	10·70	(see text)	**C₂H₅O⁺** 0·9±·2	0·8±·8	(see text)	(see text)	
CH₃OCH₂Cl→C₂H₅O⁺+Cl / C₂H₅ONO→C₂H₅O⁺+NO	{11·25 ᵘ / 10·96 ⁱ / 10·50 ᵛ / 11·5 ⁱ	11·30 / 10·79±0·00 / 10·43±·10	11·17 / 10·65 / 10·43	1·2±·2 / 1·9±·2 / 1·5±·2	2·4±·8 / 3·2±·3 / 2·4±·5	31±10 / 29±3 / 25±5	141±10 / 136±3 / 171±5	
CH₃COCH₃→CH₃CO⁺+CH₃ / CH₃COCl→CH₃CO⁺+Cl	{11·30 ᵏ / 11·16 ⁱ / 11·24 ᵉ / 11·9 ᵈ	11·32 / 11·25	11·26 / 11·23	**CH₃CO⁺** 1·3±·2 / 2·1±·2	2·5±·4 / 3·6±·4	26±3 / 24±3	148±3 / 148±3	
CH₃COOH→CH₃CO⁺+OH	11·85 ᵏ	11·75	11·83	1·3±·2	2·3±·4	18±3	142±3	
CH₃COOH→COOH⁺+CH₃		12·27±·05	12·27	**COOH⁺ HCO** 0·7±·2	0	0	145	
HCO₂CH₃→CH₃O⁺+HCO	{12·35 ᵃ / 12·4 ᵇ / 11·55 ᵍ / 11·4 ᵐ	12·0 ᶜ / 12·1 ᵐ / 11·7 ᵇ	12·23	12·21	1·7±·2	2·7±·4	21±3		7±3
HCO₂C₂H₅→C₂H₅O⁺+HCO		11·34	11·50	1·4±·2	2·2±·5	26±6		9±6
CH₃CHO→CH₃⁺+HCO	13·12 ʰ	14·53	14·53	≤1·0	≤1·0	≤7		27-34 (see text)
C₂H₅CHO→C₂H₃⁺+HCO	{13·72 ᵍ / 13·69 ᵃ	13·64	13·68	1·5±·2	2·1±·4	16±3		8±3
HCO₂CH₃→HCO⁺+CH₃O		13·47±·05	13·47	**CH₃O** 2·4±·2	3·9±·3	31±3		−2±3
CH₃CO₂CH₃→CH₃CO⁺+CH₃O		11·37±·05	11·37	1·2±·2	1·6±·4	19±5		−3±5
CH₃ONO→NO⁺+CH₃O	11·07 ᵘ	11·15	11·11	1·2±·2	1·5±·4	10±3		−4±3
CH₃OCH₃→CH₃⁺+CH₃O		14·93±·13	14·93	2·2±·3	2·8±·4	26±4		11±4
C₂H₅OH→CH₃⁺+CH₂OH	{15·5 ⁿ / 15·6 ⁱ	14·70±·10	14·70	2·0±·4	2·5±·5	23±5		−1±5
C₂H₅ONO→NO⁺+C₂H₅O	10·75 ⁱ	11·69±·05	11·69	**C₂H₅O** 1·3±·2	1·6±·3	17±4		−6±4
CH₃OC₂H₅→CH₃⁺+CH₃OCH₂		15·02	15·02	2·1±·2	2·5±·3	33±4		0±4
CH₃COCH₃→CH₃⁺+CH₃CO	15·20 ᵏ	15·36	15·28	**CH₃CO** 3·2±·2	3·9±·3	41±5		−2±5
CH₃COOH→CH₃⁺+COOH / HCO₂CH₃→CH₃⁺+HCO₂		14·0±·15 / 13·71±0·00	14·0±·15 / 13·71	**COOH** 1·7±·2 / ≤1·9	2·0±·3 / ≤2·2	16±3 / ≤17		−58±4 / ≥−46 (see text)

ᵃ R. I. Reed and M. B. Thornley, Trans. Faraday Soc., 1958, 54, 949; ᵇ A. B. King and F. A. Long, J. Chem. Phys., 1958, 29, 374. ᶜ C. E. Brion and W. J. Dunning, Trans. Faraday Soc., 1963, 59, 647; ᵈ D. N. Shigdrin, A. D. Filyugina and V. K. Potapov, Teor. Eksper. Khim., 1966, 2, 554; ᵉ McDowell and Wood, Mass Spectrometry (Inst. of Petroleum, London, 1952); ᶠ T. Kambara and I. Kanomata, Proc. Phys. Soc. Japan, 1949, 4, 71; ᵍ T. W. Shannon and A. G. Harrison, Can. J. Chem., 1961, 39, 1392; ʰ R. I. Reed, Trans. Faraday Soc., 1956, 52, 1195; ⁱ L. D'Or and J. Collin, Bull. Soc. Roy. Sci. Liege, 1953, 22, 285; ʲ ref. (7); ᵏ ref. (9); ᵐ ref. (8); ⁿ ref. (11); ᵖ ref. (10); q ref. (12); ʳ ref. (6); ˢ ref. (22); ᵗ ref. (19); ᵘ ref. (24); ᵛ ref. (29).

$$C_2H_5O^+$$

This ion has been the subject of several energetic and structural studies. The ion of hydroxyl carbinyl structure CH_3CHOH^+, obtained from secondary alcohols and ethanol, has $\Delta H_f \cong 144$ kcal/mole [8, 9]. The best value is probably the photo-ionization result of Rafaey and Chupka,[12] giving $\Delta H_f = 141$ kcal/mole. We have checked these values by measuring the translational energy of $C_2H_5O^+$ from isopropanol. Within experimental error $\bar{\varepsilon}_t$ is zero, so the photo-ionization value will be adopted.

From isotopic labelling studies [22] the $C_2H_5O^+$ ion from ethyl formate has been postulated to have hydroxy carbinyl structure. The neutrals were assumed to be $H+CO$ because this gave the heat of formation of the ion to be near that for the hydroxy carbinyl structure. We have found that there is excess energy involved in the appearance potential and the neutral must be the formyl radical since the calculated heat of formation of the ion would be much too low, even for the $C_2H_4OH^+$ structure, if the neutrals were $H+CO$.
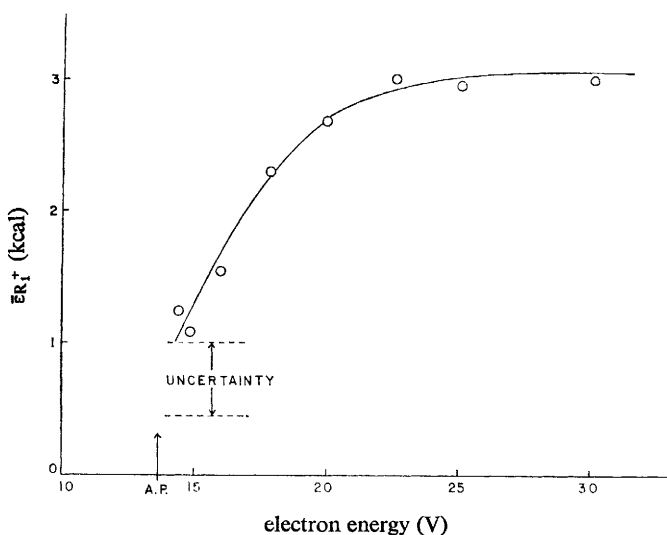

FIG. 1.—Translational energy of CH_3^+ from acetaldehyde showing extrapolation error.

Shannon and McLafferty [23] examined the decomposition of the mass 45 ion from compounds of structure YCH_2—O—CH_3 and concluded that it has the structure CH_3—O—CH_2^+. Martin, Lampe and Taft [24] and Harrison et al.[9] measured the appearance potentials of this ion from dimethyl ether and methyl ethyl ether, concluding that $\Delta H_f(CH_3$—O—$CH_2^+) = 170$ kcal/mole. We find that the mass 45 ions from methyl ethyl ether and chloromethyl methyl ether have heats of formation ca, 140 kcal/mole, corresponding to that of the CH_3CHOH^+ ion from alcohols. We do not wish to imply that $CH_3OCH_2^+$ is not produced in these compounds at all. Indeed, the decomposition studies of ref.[23] appear to offer clear evidence that it is the dominant ion at high excitation energies. However, our data indicate that the threshold process is a rearrangement instead of simple bond scission. Therefore, the heat of formation of $CH_3OCH_2^+$ is probably greater than 170 kcal/mole, if it actually exists.

The $C_2H_5O^+$ from ethyl nitrite is the only ion of this composition not yielding the hydroxy carbinyl ion energy. Even after correcting for 25 kcal of excess energy,

the heat of formation comes out to be 171 kcal/mole, 28 kcal too high. This may be a case where eqn. (3) does not hold. Another possibility is that the appearance potential data correspond to the CH_3NO^+ ion, which also has a mass of 45. Since the H_3O^+ ion is observed in the spectrum, the high value may correspond to the protonated ethylene oxide structure,

$$
\begin{array}{ccc}
H & & H \\
\diagdown & & \diagup \\
& C\!-\!C & \\
\diagup\quad\diagdown\!\!\!\diagup\quad\diagdown & \\
H \quad\ O_+ \ \quad H & \\
& | & \\
& H &
\end{array}
\qquad (I)
$$

which has been postulated as an intermediate in H_3O^+ formation from alcohols.[23, 25] Taking the heat of formation of (I) as 171 kcal/mole, we find the proton affinity of ethylene oxide to be 183 kcal/mole, a value in good agreement with that found for most oxygen-containing compounds.[8, 9]
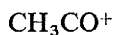
CH_3CO^+

Majer, Patrick and Robb[13] found $\Delta H_f(CH_3CO^+) = 171$ kcal/mole from appearance potentials of various carbonyl compounds. From acetic acid, acetone and acetyl chloride we find $\Delta H_f = 146 \pm 3$ kcal/mole, although our appearance potentials are almost the same as theirs. Thus, about 1 eV excess energy is involved in the dissociation of these molecular ions although it involves only simple bond scission. Photo-ionization of acetone[14] gives an appearance potential for CH_3CO^+ of 10·45 instead of 11·30 eV as found by electron impact. This is direct evidence that most of the excess energy arises from a vertical transition. The remaining excess energy 0·28 eV, is nearly identical with the calculated " kinetic shift " for this dissociation, 0·25 eV.[14] This appears to be an indirect confirmation of the validity of these kinetic shift calculations and, hence, of the statistical theory of mass spectra.

$COOH^+$

Pritchard, Thynne and Harrison[15] studied formic-d acid (DCO_2H) and found an appearance potential of 12·4 eV for DCO_2^+ and 12·8 eV for CO_2H^+, implying that the DCO_2^+ is the lower energy form of this ion with a maximum $\Delta H_f = 143$ kcal/mole. Our measurements on acetic acid show that the mass 45 ion is formed with no excess energy within experimental error. The appearance potential gives $\Delta H_f = 145$ kcal/mole. The expected structure of this ion would be $COOH^+$ instead of HCO_2^+, unless a rearrangement occurs.

HCO

Two conflicting values for the heat of formation of the formyl radical have been found by kinetics. Klein and Schoen[16] found $D(CHO\!-\!H) = 77$ kcal/mole, giving $\Delta H_f(HCO) = -3$ kcal/mole. Calvert[17] found $D(CHO\!-\!H) = 91$ kcal/mole, leading to $\Delta_f(HCO) = 11$ kcal/mole. Kerr,[18] arguing by structural analogy, suggests $\Delta H_f(HCO)$ should be 8 ± 2 kcal/mole. Reed and Brand[19] measured the ionization potential of HCO directly and combined the results with the appearance potential of HCO^+ from formaldehyde to find $\Delta H_f(HCO) = \cdot -4$ to -9 kcal/mole, Shannon and Harrison[20] found $\Delta H_f(HCO) = 0 \pm 3$ kcal/mole from appearance potentials alone.

From acetaldehyde we find a high appearance potential for CH_3^+, in agreement with Shannon and Harrison, that cannot be accounted for as excess energy. As they suggested, the neutral species are probably CO and H instead of HCO, although it could be the electronically excited HCO radical.[21]   The CH_3O^+ from methyl formate arises primarily by elimination of H and CO instead of HCO.[22]   Elimination of HCO would likely be the lowest energy process, however, and our measurements indicate that this is the case. Averaging the results from methyl and ethyl formates and acrolein gives $\Delta H_f(HCO) = 8 \pm 3.6$ kcal/mole. This value is in essential agreement with the high value of $D(CHO—H)$ from chemical kinetics and in agreement with the conclusions of Kerr.

The ionization potential of HCO measured by Reed and Brand [19] is much too high (see table 4), thereby yielding an expectedly low value for $\Delta H_f(HCO)$. However, appearance potential measurements usually give the maximum value for the heat of formation of a dissociation product, so the low results of Shannon and Harrison deserve more comment. They measured the appearance potentials of $C_6H_5^+$ from benzaldehyde and $C_3H_7^+$ from butyraldehyde, obtaining $\Delta H_f(HCO) \sim 0$ kcal/mole. However, they assumed a value for $\Delta H_f(C_6H_5^+)$ of 301 kcal/mole which is now known to be at least 18 kcal too high.[1]   Correcting their calculations, we obtain $\Delta H_f(HCO)$ = 16 kcal/mole, a value more in line with our expectations. The only explanation of their butyraldehyde data, except experimental error, is that the appearance potential corresponded to the CH_3CO^+ ion instead of $C_3H_7^+$ as assumed. Since the heat of formation of CH_3CO^+ is 146 kcal/mole, while $\Delta H_f(C_3H_7^+)$ is 190 kcal/mole,[1] the low appearance potential would be expected if this were the case. High resolution mass spectrometry could show whether CH_3CO^+ is abundant enough to interfere.

CH_3O

Kerr [18] reviewed the kinetic determinations concerning this radical and concluded that $\Delta H_f(CH_3O) = 2 \pm 2$ kcal/mole, giving $D(CH_3O—H) = 102$ kcal. These radicals were generated by pyrolysis of methyl esters of inorganic acids and, thus, presumed to have the methoxy structure. Radicals of structure CH_2OH were obtained by Buckley and Whittle [27] from the reaction of Br atoms with methanol. The activation energy of the forward reaction was 6.2 kcal, giving $\Delta H_f(CH_2OH) \simeq -8$ kcal/mole, or $D(H—CH_2OH) = 92$ kcal. However, Shaw and Thynne,[31] investigating H abstraction by methyl radicals, found evidence that $D(CH_3O—H) \simeq D(H—CH_2OH)$. Thus, the kinetic values are still doubtful.

Our results are -4, -3 and $-2(\pm 3)$ kcal/mole for the $\Delta H_f(CH_3O)$ from three esters, and -2 ± 5 kcal/mole from ethanol. Within the limits of error, any of the radicals could have either structure. From the rearrangements found for the CH_3O^+ ion, we might expect the radical to also have the more stable carbinyl structure. However, the results reported below indicate that the neutral associated with production of NO^+ from ethyl nitrite is the ethoxy radical and not the CH_3CHOH radical. By analogy, we conclude that the neutrals from the methyl esters should be the methoxy radicals. Thus, we find $\Delta H_f(CH_3O) = -3 \pm 3$ kcal/mole. This value is below the kinetics values, but within the combined uncertainties they could be the same.

The results from dimethyl ether appear to be anomalously high, giving $\Delta H_f (CH_3O) = 11 \pm 4$ kcal/mole. Unless our experimental data are in error, a failure of the excess energy-translational energy relationship is indicated.

C_2H_5O

Thermal decompositions of ethyl nitrite and ethyl nitrate yield $\Delta H_f(C_2H_5O) =$ $-6\cdot7$ kcal/mole,[18] whereas the decomposition of diethyl peroxide gives $\Delta H_f(C_2H_5O)$ $= -4\cdot4\pm1\cdot0$ kcal/mole.[34] Our only value for this radical is -6 ± 4 kcal/mole obtained from the decomposition of ethyl nitrite.* Our value must correspond to the ethoxy radical since the heat of formation of CH_3CHOH is less than -16 kcal/mole.[28] We were unable to check this value for $\Delta H_f(CH_3CHOH)$ since isopropyl alcohol does not give sufficient methyl ion intensity to measure satisfactorily.

A third form of this radical is methoxymethyl CH_3OCH_2, for which Loucks and Laidler [29] have determined $\Delta H_f = -5\cdot0\pm1\cdot0$ kcal/mole by kinetic methods. The radical produced from dissociation of methyl ethyl ether to methyl ion could have either the ethoxy or the methyl methoxy structure.† Our measurements indicate that its heat of formation is 0 ± 4 kcal/mole. Since this value is higher than ΔH_f (ethoxy), we assume that it corresponds to the methoxy methyl radical. This leads to $D(CH_3OCH_2-H) = 96\pm4$ kcal whereas the results of Loucks and Laidler are $D(CH_3OCH_2-H) = 91\pm1$ kcal. If $D(H-CH_2OH) \simeq 96$ kcal,[31] our value is more consistent with the expected trend in bond energies, i.e., $D(CH_3OCH_2-H) > D(H-CH_2OH)$, but the results are identical within experimental error.

CH_3CO

We produced this radical only from the decomposition of acetone to $CH_3^+ +$ CH_3CO. The large excess energy results in a large uncertainty in the determination, giving $\Delta H_f(CH_3CO) = -2\pm5$ kcal/mole. Kerr [18] reviews the kinetic values and suggests -4 ± 2 kcal/mole as the best value. This is within our experimental error and probably more accurate.

COOH

The only reported value for this radical is that by Bernecker and Long [6] who measured the appearance potential of mass 29 from propanoic acid and deduced $\Delta H_f(COOH) = -39$ kcal/mole. However, this value seems unreasonable because it makes the radical unstable with respect to CO_2+H (exothermic by 3 kcal/mole). From acetic acid we find $\Delta H_f = -58\pm4$ kcal/mole, giving $D(CO_2-H) = 16\pm4$ kcal. The structure of this radical would presumably be COOH, but there is no proof of this. The isomer of acetic acid, methyl formate, apparently gives a methyl ion with elimination of CO_2 and H instead of COOH, since the heat of formation of the neutral species is $\geqslant -46$ kcal/mole while $\Delta H_f(CO_2)+\Delta H_f(H) = -42$ kcal/mole. This could indicate that the HCO_2 radical is unstable whereas the COOH structure obtained from acetic acid is stable.

These results confirm the former conclusion [2] that excess energy in electron-impact dissociations is the rule rather than the exception. Ignorance of this principle has often led to erroneous conclusions with regard to the mechanisms of fragmentations

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* A slight impurity of NO interfered with this determination and with the corresponding determination from methyl nitrite. The NO arose from pyrolysis of the nitrites on the filament in the source and, therefore, could not be eliminated. Although the appearance potentials could be determined satisfactorily from the breaks in the curves, the translational energy measurements may be influenced by the presence of the thermal NO+ from direct ionization.

† A. G. Harrison (private communication) found the ratio of $[CD_3^+]/[CH_3^+]$ ion intensity from $CD_3OC_2H_5$ to be 1·7.

as well as to the energetics. Appearance potentials combined with excess energy measurements will indeed be a valuable guide to the elucidation of mechanisms, particularly as the thermochemical data on ions and radicals are improved. However the processes occurring at threshold may not be the same as those occurring at higher excitation energies. An example is the $C_2H_5O^+$ ion from the methyl ethers; moreover, the excess energy relationship cannot be completely reliable. We have encountered at least one, and possibly three instances of its failure in this study, out of a total of 29 dissociations. Certainly, all the methods of mass spectrometry must be used in order to attack the complexities of fragmentations.

TABLE 2.—SUMMARY OF THERMOCHEMICAL DATA OBTAINED IN THIS WORK

species	this work	ΔH_f in kcal/mole		"best" value
		other	(method) *	
HCO^+	198 ± 2	235 [a]	(1)	198 ± 2
		207 [b]	(2)	
CH_2OH^+	170 ± 5	170 ± 1 [c]	(3)	170 ± 1
CH_3CHOH^+	~ 140	141 ± 1 [c]	(3)	141 ± 1
CH_3CO^+	146 ± 3	171 [d]	(2)	146 ± 3
		149 [e]	(3)	
		189 [f]	(1)	
$COOH^+$	} 145	152 [g]	(2)	} 145
HCO_2^+		143 [g]	(2)	
HCO	8 ± 3	-3 [h]	(4)	8 ± 3
		11 [i]	(4)	
		0 ± 3 [j]	(2)	
CH_3O	-3 ± 3	2 ± 2 [k]	(4)	0 ± 3
CH_2OH	-1 ± 5	-6 [l]	(4)	-3 ± 4
		-1 [q]	(4)	
C_2H_5O	-6 ± 4	-7 ± 2 [k]	(4)	-6 ± 2
		$-4 \cdot 4 \pm 1 \cdot 0$ [r]	(4)	
CH_3OCH_2	0 ± 4	-5 ± 1 [m]	(4)	-4 ± 2
CH_3CO	-2 ± 5	-4 ± 2 [k]	(4)	-4 ± 2
		-5 [n]	(3)	
$COOH$	-58 ± 4	-39 [p]	(2)	-58 ± 4

* Method (1): direct measurement of ionization potential combined with heat of formation of radical; method (2): electron impact measurements of appearance potentials of fragment ions; method (3): photoionization appearance potentials of fragment ions; method (4): general kinetics methods.

[a] ref. 19. The $\Delta H_f(HCO)$ as obtained in this work was used. [b] ref (7); [c] ref. (12); [d] ref. (13); [e] ref. (14); [f] ref. (19); [g] ref. (15); [h] ref. (16); [i] ref. (17); [j] ref. (20); [k] ref. (18); [l] ref. (27); [m] ref. (29); [n] ref. (18) and ref. (30); [p] ref. (6); [q] ref. (31); [r] ref. (34).

A method which may be only 90 % reliable will still be valuable in studies of the energies of radicals and ions. A summary of our results is given in table 2 along with the results of other methods. For CH_2OH^+ and $C_2H_4OH^+$ our work provides only a confirmation and the more precise results obtained by photo-ionization are considered the " best " values. For the other ions, and for the HCO and COOH radicals, our values are taken. Our results for all the other radicals are compatible with the values obtained by various kinetic methods. While the precision is not as good as that from kinetics, the absolute accuracy should be as good or, in some cases, even better. The results from kinetics and our studies are thus weighted according to the stated uncertainties and averaged together to find the best values.

For most of these radicals, we have merely confirmed the established kinetic values. A notable exception is the formyl radical. The most significant aspect of this study is the demonstration that this method is competitive with even the best kinetic methods for determining bond energies. Its utility may be better appreciated for determining heats of formation of radicals such as COOH that cannot easily be examined by ordinary kinetics. And it should be indispensable for studying ions.

TABLE 3.—THERMOCHEMICAL DATA USED IN THIS WORK [a]

species	ΔH_f° (kcal/mole)	species	ΔH_f (kcal/mole)
HCOOH	$-90{\cdot}5$	$CH_3CHOHCH_3$	$-65{\cdot}5$
CH_3CHO	$-39{\cdot}7$	CH_3OCH_2Cl	-52 [c]
CH_2CHCHO	-23	$HCO_2C_2H_5$	-89
CH_3CH_2OH	$-56{\cdot}2$	OH	$9{\cdot}3$
CH_3ONO	$-14{\cdot}9$ [b]	H	$52{\cdot}1$
C_2H_5ONO	$-24{\cdot}2$ [b]	CH_3	34 [d]
CH_3OCH_3	$-44{\cdot}0$	C_2H_3	65
HCO_2CH_3	$-83{\cdot}7$	NO	$21{\cdot}6$
$CH_3OC_2H_5$	$-52{\cdot}1$	C_2H_5	25
CH_3COOH	-104	Cl	29
CH_3COCH_3	$-51{\cdot}9$	CH_3^+	261 [e]
CH_3COCl	$-58{\cdot}2$	$C_2H_3^+$	269
$CH_3CO_2CH_3$	$-99{\cdot}2$	HCO^+	198 [f]
CH_3CHOH	-16 [g]	CH_2OH^+	170 [f]
		CH_3CHOH^+	141 [f]
		CH_3CO^+	146 [f]

[a] All values except those noted were taken from ref. (1); [b] ref. (26); [c] estimated by group orbital method of J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 339; [d] ref. (18); [e] obtained by combining the spectroscopic ionization potential of CH_3 (ref. (21)) with the heat of formation of the methyl radical; [f] this work; [g] ref. (28).

TABLE 4.—IONIZATION POTENTIALS OF RADICALS

radical	ionization potential (eV) derived	expt.	ref.
HCO	$8{\cdot}24 \pm {\cdot}13$	$9{\cdot}88 \pm {\cdot}05$	19
CH_2OH	$7{\cdot}51 \pm {\cdot}2$	$8{\cdot}14 \pm {\cdot}15$	35
CH_3CHOH	$6{\cdot}81 \pm {\cdot}1$		
CH_3CO	$6{\cdot}51 \pm {\cdot}13$	$8{\cdot}08 \pm {\cdot}09$	19
COOH	$8{\cdot}80 \pm {\cdot}2$		

Table 4 lists the adiabatic ionization potentials of the radicals as derived from the differences in heats of formation of the radicals and corresponding ions. The discrepancy for CH_2OH is about the same as for many electron impact determinations of radical ionization potentials. However, the discrepancies of $I(HCO)$ and $I(CH_3CO)$ are considerably above normal experimental error. Reed and Brand did report unusual difficulties in these determinations.[19] In addition, the ground state configuration of HCO^+ is linear, whereas the ground state configuration of HCO is bent.[21] Thus, direct ionization of the radical should give a vibrationally excited ion. The acetyl radical and ion should have similar structures.

Another aspect of potential importance is that in several of these dissociations, there is enough excess energy available so that the neutral species may decompose further. For example, in reaction 20 in table 1, there is $31-4 = 27$ kcal to be distributed among the vibrational degrees of freedom of the products, CH_3O and HCO^+.

If this energy is distributed in proportion to the relative number of vibrational degrees of freedom of each product, the CH_3O radical would have 20 kcal excitation energy, more than enough to enable it to decompose to the formyl radical and hydrogen. This assumption of equipartition of energy has been widely applied in the statistical theory of mass spectra and McLafferty and Pike [32] have found direct proof of its validity. Eqn. (3) is apparently applicable to the first step of a two-step dissociation process. This was assumed without proof in a previous publication.[33] Extension of the methods of this work to two-step dissociations should be practicable.

CONCLUSIONS

Excess energy measurements have been shown to be necessary for studying appearance potentials of fragmentations induced by electron impact. When excess energy is included, the method is capable of yielding good values for the heats of formation of radicals and ions.

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