the two-stage behavior has essentially disappeared. However, it must be emphasized that these explanations as well as the specific interpretation of the parameter β are somewhat speculative and need to be checked by further experiments.

ITHACA, NEW YORK

Free Radicals by Mass Spectrometry. XVII. Ionization Potential and Heat of Formation of Vinyl Radical

BY A. G. HARRISON[1] AND F. P. LOSSING

The vertical ionization potential of vinyl radical is found to be 9.45 v. by direct electron impact on radicals produced by the thermal decomposition of methyl vinylmercury. From the appearance potential of vinyl ion from ethylene, $D(C_2H_3-H)$ = 105 ± 3 kcal./mole, $\Delta H_f(C_2H_3)$ = 65 ± 3 kcal./mole, $\Delta H_f(C_2H_3{}^+)$ = 283 ± 3 kcal./mole and $D(C_2H_2-H)$ in vinyl radical is 41 ± 3 kcal./mole.

Introduction

As pointed out recently by Cottrell,[2] the published electron impact measurements of the C–H bond dissociation energy in ethylene show a large discrepancy, the two values being $D(C_2H_3-H)$ = 91.5 kcal./mole[3] and 122 kcal./mole.[4] The corresponding values for $\Delta H_f(C_2H_3)$ are 51.6 and 82 kcal./mole. There are a number of reasons for preferring a value for $D(C_2H_3-H)$ somewhat larger than $D(C_2H_5-H)$ (~96[2]) but not larger than $D(C_6H_5-H)$, for which values in the range 102–107 have been obtained.[2] When used to calculate the dissociation energy of the central C–C bond in 1,3-butadiene, the two values of $\Delta H_f(C_2H_3)$ lead to $D(C_2H_3-C_2H_3)$ = 77 and 138 kcal./mole, both of which appear quite improbable by comparison with other C–C bonds.[5] Recently[6] support for the higher value for $\Delta H_f(C_2H_3)$ has been withdrawn, on the basis of a revised value for $\Delta H_f(t$-butyl$^+)$. Since considerable evidence supports a value of $\Delta H_f(C_2H_3{}^+)\sim283$ kcal./mole,[4] it would appear that a direct determination of the ionization potential of the C_2H_3 radical should be of assistance in resolving this discrepancy in the data for ΔH_f-(C_2H_3).

Experimental

Although the vinyl radical had been detected by mass spectrometry in the thermal decomposition of divinyl ether,[7] considerable difficulty was encountered in producing the radical in yields sufficient to permit measurement of the ionization potential. A much higher yield of vinyl has now been obtained by the pyrolysis of methyl vinylmercury. This compound was prepared by the reaction between vinylmagnesium bromide and methyl mercuric iodide in tetrahydrofuran.[8] It was purified by repeated vacuum distillation until the mass spectrum showed only negligible traces of impurities, mainly di-methyl and divinylmercury.[9]

Pyrolysis of methyl vinylmercury in a fused silica capillary furnace leading to the ionization chamber of a mass spectrometer[10] resulted in the formation of vinyl and methyl radicals, as shown by large increases in the mass 27 and mass 15 peaks when using electrons of low energy. Other products were acetylene, ethane and a small amount of methane. No significant amounts of the dimerization products 1,3-butadiene and propylene were found. At furnace temperatures above 900°, the yield of vinyl radicals decreased rapidly, with the formation of large quantities of acetylene.

The method of comparison of the ionization efficiency curve for vinyl radical with that for the added standard gas, in this case krypton, was the same as that employed to measure the ionization potentials of propyl and butyl radicals.[11] As a check on the calibration procedure, a number of curves also were obtained for the acetylene which was formed in the reaction.

In mixtures of ethylene and krypton, the ionization efficiency curves for krypton and for the $C_2H_3{}^+$ ion from ethylene were measured down to the "vanishing" point, where the ion current was 0.01% of the ion current with 50 v. electrons. The voltage difference between these curves at corresponding ion currents was found to decrease from 0.25 v. at 0.1% of the 50 v. ion current to 0.05 v. at 0.01%. Owing to this lack of parallelism, $A(C_2H_3{}^+)$ was evaluated by extrapolation of a plot of voltage difference against ion current[12] as shown in Fig. 1. The average of a number of determinations, 14.00 ± 0.05 v., was essentially the same as that obtained by the "vanishing current" method.[13] Unless some drastic alteration in the shape of this curve occurs in the region of very small ion currents below 0.01%, it is difficult to see how the extrapolated voltage difference (Fig. 1) can differ from 0.00 v. by more than ± 0.05 v. Owing to the curvature observed. however, a larger limit of error has been assigned, and $A(C_2H_3{}^+)$ from ethylene has been taken as 14.00 ± 0.1 v., in excellent agreement with 14.04 ± 0.1 v. as found by Field[4] and with the average of two earlier determinations of 14.2 ± 0.1[14] and 13.92 v.[15]

Results and Discussion

The average of several sets of ionization efficiency curves for the vinyl radical and for krypton gave 9.45 ± 0.05 v. for the ionization potential of vinyl radical. On the same scale, the curves for the acetylene formed in the reaction gave 11.42 ± 0.05 v. for $I(C_2H_2)$, in good agreement with three identical values of 11.41 v. obtained by electron impact,[16] by photoionization[17] and by spectros-

(1) National Research Council post-doctorate fellow 1957–1959.

(2) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958.

(3) D. P. Stevenson, THIS JOURNAL, **65**, 209 (1943).

(4) F. H. Field, J. Chem. Phys., **21**, 1506 (1953).

(5) J. Collin and F. P. Lossing, Can. J. Chem., **35**, 778 (1957).

(6) F. W. Lampe and F. H. Field, THIS JOURNAL, **81**, 3238 (1959).

(7) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, "Applied Mass Spectrometry," Institute of Petroleum, London, 1954, p. 102.

(8) B. Bartocha, F. E. Brinckman, H. D. Kaesz and F. G. A. Stone, Proc. Chem. Soc. (London), 116 (1958).

(9) We are indebted to Dr. L. C. Leitch and Mr. D. Kovachic for this preparation.

(10) J. B. Farmer and F. P. Lossing, Can. J. Chem., **33**, 861 (1955).

(11) F. P. Lossing and J. B. de Sousa, THIS JOURNAL, **81**, 281 (1959).

(12) J. W. Warren, Nature, **165**, 810 (1950).

(13) For a discussion of various methods for evaluating appearance potentials see reference 21.

(14) P. Kusch, A. Hustrulid and J. T. Tate, Phys. Rev., **52**, 843 (1937).

(15) J. J. Mitchell and F. F. Coleman, J. Chem. Phys., **17**, 44 (1949).

(16) R. E. Honig, ibid., **16**, 105 (1948).
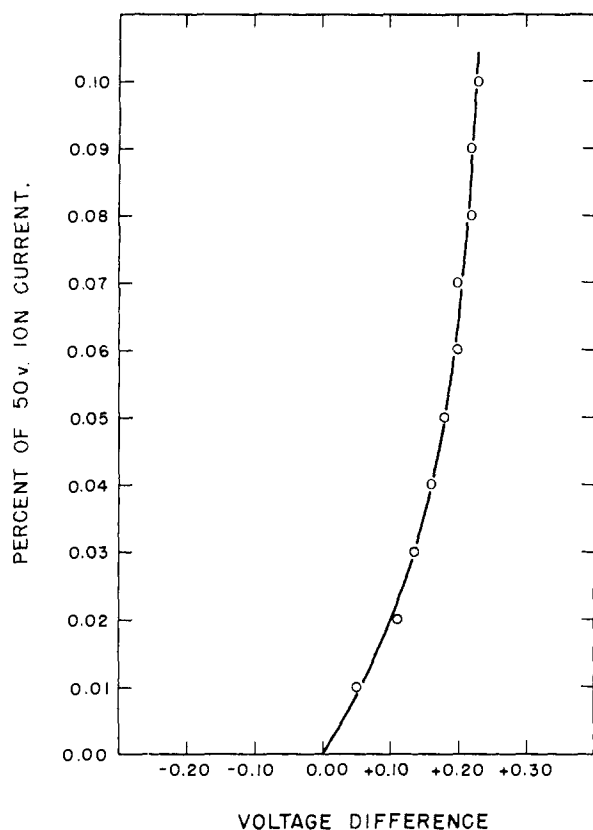
(17) K. Watanabe, ibid., **26**, 542 (1957).

VOLTAGE DIFFERENCE

Fig. 1.—Voltage difference between ionization efficiency curves for Kr^+ and for $C_2H_3^+$ from ethylene as a function of ion current.

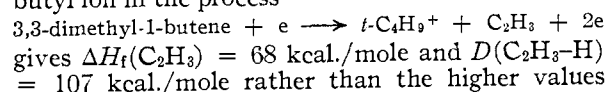copy,[18] indicating that the electron energy scale was correctly established. This value for I-(C_2H_3) lies between the earlier results 9.87 ± 0.2 v.[3] and 8.69 v.,[4] which were obtained by the indirect method from the appearance potentials of fragment ions in hydrocarbons. It is nearly the same as a value of 9.37 ± 0.2 v., for which a preliminary announcement has been published[19] but without particulars as to whether it is a direct or indirect measurement.

On the assumption that the observed threshold of 14.0 v. for the process

$$C_2H_4 + e \longrightarrow C_2H_3^+ + H + 2e$$
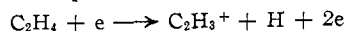
corresponds to a dissociation with no excitational or kinetic energy, one obtains $D(C_2H_3-H) = A(C_2H_3^+) - I(C_2H_3) = 105 \pm 3$ kcal./mole. From $\Delta H_f(C_2H_4) = 12.5$ kcal./mole,[20] this value leads to $\Delta H_f(C_2H_3) = 65 \pm 3$ kcal./mole and ΔH_f-$(C_2H_3^+) = 283 \pm 3$ kcal./mole.

Lampe and Field have pointed out[6] recently that, on the basis of a revised value for the heat of formation of t-butyl ion, the appearance potential of t-butyl ion in the process

$$3,3\text{-dimethyl-1-butene} + e \longrightarrow t\text{-}C_4H_9^+ + C_2H_3 + 2e$$

gives $\Delta H_f(C_2H_3) = 68$ kcal./mole and $D(C_2H_3-H) = 107$ kcal./mole rather than the higher values

(18) W. C. Price, Phys. Rev., 47, 444 (1935).

(19) R. I. Reed and M. B. Thornley, Trans. Faraday Soc., 54, 949 (1958).

(20) F. D. Rossini, et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

proposed earlier.[4] These values are in good agreement with those obtained by the direct method in the present work. However, some support for the earlier high value for $\Delta H_f(C_2H_3)$ has been presented by Reed and Thornley[19] from the difference in the appearance potentials for the processes

$$HCHO + e \longrightarrow HCO^+ + H + 2e$$

$$C_2H_5CHO + e \longrightarrow HCO^+ + C_2H_5 + 2e$$
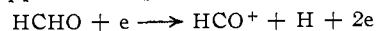
It should be noted, however, that according to Stevenson's rule[21] $A(HCO^+)$ in the second of these two processes will include excitational energy of the fragments, since the ionization potential of HCO $(9.87$ v.$)^{22}$ is greater than that of C_2H_3. There is a strong possibility, therefore, that a heat of formation of C_2H_3 based on the difference in appearance potentials will be too high as a consequence of such excitational energy. Moreover, using Reed's values $I(C_2H_3) = 9.37$ v. and ΔH_f-$(C_2H_3) = 77.7$ kcal./mole, $\Delta H_f(C_2H_3^+)$ should be 294 kcal./mole. On this basis a minimum value for the appearance potential of $C_2H_3^+$ from ethylene would be 14.5 v., that is, 0.5 v. higher than the observed value. Since cases of ion pair formation in hydrocarbons yielding H^- are rare or non-existent,[23] there is no reasonable basis for supposing that $C_2H_3^+$ could be formed from C_2H_4 at energies less than that required for the process

$$C_2H_4 + e \longrightarrow C_2H_3^+ + H + 2e$$
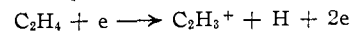
The electron impact data for $\Delta H_f(C_2H_3^+)$ have been discussed by Field.[4] Appearance potentials for $C_2H_3^+$ from ethylene, n-butane, 1-butene and ethane give $\Delta H_f(C_2H_3^+) = 281-284$ kcal./mole. Vinyl and ethyl chloride, from which Cl^- ion formation may occur, give a lower value, $\Delta H_f(C_2H_3^+) = 274-277$ kcal./mole. Propylene gives a consider-

TABLE I

BOND DISSOCIATION ENERGIES BASED ON $\Delta H_f(C_2H_3) = 65 \pm 3$ KCAL./MOLE

Bond	Diss. energy ($\pm$ 3 kcal./mole)
C_2H_3–H	105
C_2H_3–CH_3	92.5
C_2H_3–C_2H_3	104 ($\pm$ 6)
C_2H_3–Cl	85.5
C_2H_3–Br	73.4
C_2H_3–H	41

ably higher value, 292 kcal./mole. Although in this process the conditions of Stevenson's rule are fulfilled, namely, that $I(C_2H_3) < I(CH_3)$, it should be noted that, contrary to the interpretation sometimes placed upon it, the rule does not state that the fragments R_1^+ and R_2 will necessarily be formed with no excitational energy if $I(R_1) < I(R_2)$, but that unless this condition is met there will be excitational energy. Leaving aside the propylene value, the good agreement of the values for ΔH_f-$(C_2H_3^+)$ from the dissociation of n-butane, 1-butene and ethane with that obtained from the simplest dissociation process, that of ethylene, lead us to accept $\Delta H_f(C_2H_3^+) = 283 \pm 3$ kcal./mole in agreement with Field.[4]

(21) D. P. Stevenson, Disc. Faraday Soc., 10, 35 (1951).

(22) R. I. Reed, Trans. Faraday Soc., 52, 1195 (1956).

(23) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

The dissociation energies of a number of C_2H_3–R bonds derived from $\Delta H_f(C_2H_3) = 65 \pm 3$ kcal./mole are given in Table I. Heats of formation used are: ethylene 12.5,[20] propylene 4.88,[20] 1,3-butadiene 26.33,[20] vinyl chloride 8.89,[24] vinyl bromide 18.68[25] and acetylene 54.2.[20] The calculation of the C–H bond in vinyl radical itself reveals that the thermal stability of vinyl is probably not much greater than that of ethyl $(D(C–H) \sim 39$ kcal./mole) or t-butyl $(D(C–H) \sim 42$ kcal./mole),[26] assuming

(24) J. R. Lacher, E. Emery, E. Bohmfalk and J. D. Park, *J. Phys Chem.*, **60**, 492 (1956).

(25) J. R. Lacher, A. Kianpour and J. D. Park, *ibid.*, **61**, 1125 (1957).

that the activation energies for the reverse reactions of H with the olefins and with acetylene are not greatly different.

It is interesting to note that the presently obtained values of $\Delta H_f(C_2H_3) = 65$ kcal./mole, $D(C_2H_3–H) = 105$ kcal./mole and $D(C_2H_3–Cl) = 85$ kcal./mole are almost identical with the estimates of 64, 104 and 86 kcal./mole, respectively, made some years ago by Szwarc.[27]

(26) Based on preferred values of $D(R–H)$ given in ref. 2 and standard heats of formation of corresponding olefins.

(27) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

OTTAWA, CANADA

Electron-Spin Resonance Studies of Anionic Polymerization

BY M. LEVY AND M. SZWARC

Anionic polymerization of styrene was investigated by means of an electron-spin resonance spectrograph. No signal is shown by the solution of "living" polystyrene initiated by metallic potassium or by sodium salt of α-methylstyrene "tetramer." On the other hand, a signal, identified as that of sodium naphthalene, is shown by the solution of "living" polystyrene initiated by this reagent. Intensity of this signal was studied as a function of monomer to initiator ratio, M_{total}/I_{total}, and of temperature, and it was concluded that it arises from an incomplete consumption of initiator in the polymerization process. Furthermore, it was shown that some step of the initiation process is slow in comparison to an electron transfer process and corresponds to a higher activation energy than the propagation reaction. The nature of this step was investigated. Preliminary studies of the depropagation reaction are reported.

Two mechanisms of anionic polymerization initiation are known: the addition of a negative ion to a monomer, and the transfer of an electron from an electron donor, D or D^-, to a monomer M.[1,2] The latter mode of initiation is represented by the equations

$$D + M \longrightarrow D^+ + M^-$$

or

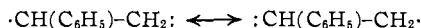$$D^- + M \longrightarrow D + M^-$$
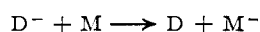
where M^- represents the primary radical-ion formed in the electron transfer process.

The primary radical-ion M^- is neither a conventional radical nor a carbanion although its structure might be represented by the two resonating forms illustrated with styrene as an example

$$\cdot CH(C_6H_5)–CH_2: \longleftrightarrow : CH(C_6H_5)–CH_2\cdot$$

which imply that one end of M^- acts as if it were a radical while the other acts as if it were a carbanion or *vice versa*. However, on addition of one monomer molecule to M^- a dimer is formed, possessing one "true" radical end and one "true" carbanion end, no direct interaction taking place between these two centers, *e.g.*

$$(C_6H_5)CH=CH_2^- + C_6H_5CH=CH_2 \longrightarrow$$
$$\cdot CH(C_6H_5)–CH_2–CH_2–CH(C_6H_5)^-.$$
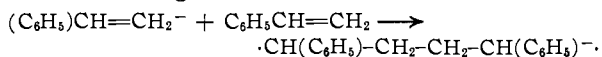
Such a dimer can result in a further polymerization of a dual character: the radical end might grow according to the rules of radical mechanism while the growth of the carbanion end would be determined by the laws of anionic polymerization. Indeed, the

(1) M. Szwarc, M. Levy and R. Milkovich, THIS JOURNAL, **78**, 2656 (1956).

(2) M. Szwarc, *Nature*, **178**, 1168 (1956).

work of Tobolsky and his students[3] indicated that such a situation exists in copolymerization of styrene and methyl methacrylate initiated by the dispersion of metallic lithium.

Monomeric radical-ions, M^-, may also dimerize and form dimeric di-carbanions, *e.g.*

$$2CH(C_6H_5)=CH_2^- \longrightarrow {}^-CH(C_6H_5)–CH_2–CH_2–CH(C_6H_5)^-$$
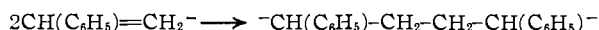
and these may continue their growth by anionic mechanism only. Whether the reaction follows this course or the one discussed in the preceding paragraph depends on the conditions of the polymerization. For example, a homogeneous initiation of styrene polymerization by sodium naphthalene is a very rapid process; it produces, therefore, a comparatively high concentration of styrene$^-$ radical-ions, favoring therefore their dimerization to di-carbanions.[1,2] On the other hand, the slow heterogeneous initiation by metallic lithium dispersion, particularly if carried out in high concentration of monomer, favors the formation of the dimeric radical-ions. The importance of the rate of initiation in determining the nature of the primary species is shown clearly by recent results of Tobolsky, *et al.*,[3a] who repeated their experiments with styrene–methyl methacrylate mixture, initiating, however, the polymerization by sodium dispersion. Under this condition only methyl methacrylate polymerized. This can be explained by more rapid initiation by sodium as

(3) K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **31**, 123 (1958); K. F. O'Driscoll, R. J. Boudreau and A. V. Tobolsky, *ibid.*, **31**, 115 (1958).

(3a) A. V. Tobolsky, D. J. Kelley, K. F. O'Driscoll and C. E. Rogers, *J. Polymer Sci.*, **28**, 425 (1958).