

# FREE RADICALS BY MASS SPECTROMETRY

# VII. THE IONIZATION POTENTIALS OF ETHYL, ISOPROPYL, AND PROPARGYL RADICALS AND THE APPEARANCE POTENTIALS OF THE RADICAL IONS IN SOME DERIVATIVES<sup>1</sup>

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#### ABSTRACT

The ionization potentials of ethyl, isopropyl, and propargyl radicals have been measured by electron impact on radicals produced by thermal decomposition of appropriate compounds. The values are:ethyl  $8.78\pm0.05$  ev., isopropyl  $7.90\pm0.05$ ev, and propargyl  $8.25\pm0.08$  ev. From the appearance potentials of these ions in various compounds, the following values of bond dissociation energies were obtained:

$D(C_2H_5-H)$	$= 98.5 \pm 2.3$ ,	D(s-C	<sub>3</sub> H <sub>7</sub> H)	$= 86.7 \pm 2.3$	3.
$D(s-C_3H_7-I)$	$= 42.4 \pm 2.3$ ,	$D(s-C_3)$	$H_7 - Br$	$= 58.8 \pm 2.3$	3,
$D(s-C_3H_7-C_1)$	$= 73.3 \pm 2.3$	D(CH:C)	$CH_2 - I$	$= 45.7 \pm 3.2$	Ż,
$D(CH:C.CH_2-Br)$	$= 57.9 \pm 3.2$	kcal./mole,	assuming	no kinetic	energy
of the products.			5		

# INTRODUCTION

The ionization potential of the ethyl radical was measured by Fraser and Jewitt (5) by directing a beam of ethyl radicals and other products from the decomposition of lead tetraethyl into an ionization gauge detector. They found  $I(C_2H_5) = 10.6 \pm 0.8$  ev., a value which was undoubtedly too high because of the presence of reaction products such as ethylene. Hipple and Stevenson (7) measured the ionization potential of the ethyl radical by electron impact on radicals produced by the thermal decomposition of lead tetraethyl in a quartz capillary furnace opening into the ionization chamber of a mass spectrometer. By this means they found  $I(C_2H_5) = 8.67 \pm 0.1$  ev., a value which, taken in conjunction with the appearance potential of  $C_2H_5^+$  in the mass spectrum of ethane,  $12.92 \pm 0.1$  ev. (23), led to a dissociation energy of the C<sub>2</sub>H<sub>5</sub>—H bond of  $4.25\pm0.2$  ev. or  $98.0\pm4.6$  kcal./mole. This is in good agreement with the average electron impact value of  $4.20 \pm 0.04$  ev. (96.9  $\pm 1$  kcal./mole) recently quoted by Stevenson (21) and the value of  $98\pm 2$  kcal./mole obtained by photobromination (1).

The ionization potential of the isopropyl radical has not previously been measured directly, but a value of  $7.45\pm0.1$  ev. has been derived from the appearance potentials of  $C_3H_7^+$  in the mass spectra of isobutane, isopentane, and 2,3-dimethyl butane, the heats of formation of these compounds, and the bond dissociation energies of CH<sub>3</sub>-H and C<sub>2</sub>H<sub>5</sub>-H (20). This value, together with the appearance potential of the  $C_3H_7^+$  ion in the mass spectrum of propane,  $11.67 \pm 0.1$  ev. (24), leads to a dissociation energy for the s-C<sub>3</sub>H<sub>7</sub>—H bond of  $4.22\pm0.2$  ev. (97.3 $\pm4.6$  kcal./mole). This appears to be high by comparison with Stevenson's electron impact average of  $4.09 \pm 0.09$  ev.

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 $(94.3\pm2 \text{ kcal./mole})$  and with the Butler and Polanyi pyrolysis value of  $\sim 89 \text{ kcal./mole}$  (19).

As far as the authors are aware, no published measurements or predictions of the ionization potential of the propargyl radical  $(CH:C.CH_2)$  have been made. The radical does not appear to have been identified previously, although it has been suggested that its thermal stability might be high (27).

#### EXPERIMENTAL

### Production of the Radicals

The fact that ethyl and isopropyl radicals are much less stable thermally than methyl, allyl, or benzyl radicals, whose ionization potentials were reported in an earlier paper (13), required a modification of the reactor used previously. In a reactor of the type described in earlier papers (14, 15) the residence time was sufficiently long to allow the disappearance of an appreciable fraction of the radicals at the temperature ( $\sim 660^{\circ}$ C.) at which mercury diethyl or azoisopropane decomposed. Although these radicals were found in considerable abundance under these conditions (12), the presence of appreciable amounts of the decomposition, disproportionation, and combination products caused serious interference at the parent peak of the radical. In order to reduce this interference a furnace was constructed in which the residence time would be shorter. This furnace was similar in design to that used by Hipple and Stevenson (7) and consisted of a quartz tube of 1.5 mm. internal diameter surrounded at the end by a heater, 2 cm. in length, cut from tantalum sheet in the shape previously described (15). The heater was enclosed in a quartz sheath sealed to the end of the quartz tube. A cylindrical radiation shield of Nichrome V surrounded the sheath. The furnace was mounted coaxially with the hole in the top plate of the ionization chamber, at a distance of about 1 mm. The compound was admitted to the reactor through a molecular-flow leak without the use of helium as a carrier. With this arrangement the pressure in the reactor was very low ( $\sim 10^{-3}$  mm.) and second-order products were considerably reduced. The dissociation products of the radicals were still present but in reduced amounts.

#### (a) Ethyl Radicals

The decomposition of mercury diethyl at about 800°C. gave rise to ethyl radicals, butane, ethane, ethylene, and hydrogen. A small amount of undccomposed mercury diethyl was also present. Out of a combined peak height of 497 cm. at mass 29 using 50 ev. electrons, a net peak height of 249 cm. for the ethyl radical was obtained after subtraction of the contributions from ethane, butane,  $C^{12}C^{13}H_4$ , and mercury diethyl. The ratio of ethane to butane at 800°C. was 0.36:1. This ratio of disproportionation  $(k_1)$  to combination  $(k_2)$  (0.36) is not greatly different from that found  $(k_1/k_2 = 0.1 \text{ to } 0.3)$  at lower temperatures (2, 10). If significant, this result would suggest that

# $E_{\text{combination}} \simeq E_{\text{disproportionation}}.$

However, at the very low pressures involved ( $\sim 10^{-3}$  mm.) it is questionable whether the ethane and butane arise from homogeneous disproportionation



and combination reactions rather than from surface reactions. Some butane may also be formed directly from mercury diethyl under these conditions.

(b) Isopropyl Radicals

As in the case of ethyl, the production of a high concentration of isopropyl radicals presented experimental difficulties owing to the thermal instability of the radicals. In the high pressure reactor, the decomposition of azoisopropane in a stream of helium at 6.5 mm. was almost complete at  $665^{\circ}$ C. The increase in the mass 43 peak at low electron energies showed the isopropyl radical to be present. At this temperature some isopropyl radicals were decomposing, the products being propylene and hydrogen almost exclusively (12). By the use of a retractable furnace (9) in the high pressure reactor, the product of dimerization of the radicals was found to be mainly 2,3-dimethyl butane with a small amount of another hexane, possibly 2-methyl pentane, showing that the radicals were indeed isopropyl radicals. In the low pressure reactor, azoisopropane was 90% decomposed at 655°C. At this temperature the mass 43 peak height was 1030 cm. After subtracting the contributions from 2,3-dimethyl butane, propane, and undecomposed azoisopropane, a peak height of 329 cm. for the isopropyl radical remained.

(c) n-Propyl Radicals

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Attempts to produce the *n*-propyl radical in quantities sufficient for ionization potential measurements were unsuccessful. The decomposition of azo-*n*propane at 665°C. in the high pressure reactor resulted in the formation of methyl radicals and ethylene in approximately equal amounts, together with nitrogen, *n*-hexane, propane, propylene, and some ethane formed from the combination of the methyl radicals (12). The mode of decomposition of *n*propyl appears to be almost entirely by

 $n - C_3 H_7 \rightarrow C H_3 + C_2 H_4$ 

 $n-C_3H_7 \rightarrow C_3H_6+H.$ 

This is in agreement with conclusions drawn from kinetic studies (19).

(d) Propargyl Radicals

and not by

The decomposition of propargyl iodide at 1000–1100°C. in either the highpressure or the low-pressure reactor resulted in a good yield of propargyl radicals. The dimer, 1,5-hexadiyne, was also formed.

# Measurement of the Ionization Potentials

The method of calibrating the voltage scale using a number of standards was the same as that used previously (13). In this case the calibration line was found to have a slope of unity within the precision of measurement. Krypton was added to the gas stream as a reference standard, and the difference between the appearance potential of the radical peak and the appearance potential of the krypton mass 84 peak was determined by the method of extrapolated voltage differences (28). The net peak height for the radical ion at 50 ev. was determined by subtracting the contributions from dimers and other prod-

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ucts as described above. Ionization efficiency curves for the radical ions from these products were measured to ensure that no contributions to the peaks could occur at the low electron energies at which the voltage difference measurements were made. The only correction of this kind found to be necessary was a small correction to the krypton mass 84 peak as a result of the 2,3-dimethyl butane formed from isopropyl radicals. This correction was evaluated from measurements of the mass 84 peak in the absence of krypton, other conditions being the same.

#### Measurement of the Appearance Potentials

As found by Stevenson and Hipple (23) a significant correction to the mass 29 peak was required in the measurement of  $A(C_2H_5^+)$  from ethane. The appearance potential of  $C_2H_4^+$  from ethane is appreciably lower than that of  $C_2H_5^+$  (23). Consequently the mass 28 peak is many times as high as the mass 29 peak at electron energies a few volts above  $A(C_2H_5^+)$ . The isotopic  $C^{12}C^{13}H_4^+$  peak from  $C_2H_4^+$  was found to account for almost one-third of the mass 29 peak under these conditions. The correction to mass 29 was calculated from the natural abundance of  $C^{13}C^{13}H_4^+$  or in the ratio of formation of the ions would occur as a result of isotopic factors. This correction raised the observed value of  $A(C_2H_5^+)$  by about 0.2 ev. as was found by Stevenson and Hipple (23).

The ionization efficiency curves for  $A(C_2H_5^+)$  from the halides showed curved  $\delta V$  vs. I plots and the extrapolated values being apparently low by 0.4 to 0.6 ev. are not reported here. The cause of this discrepancy is not obvious. I<sup>-</sup> ions from the iodide were found, but only to the extent of about one part in 6000 of the  $C_2H_5^+$  ion. This amount should not appreciably lower the appearance potential, and in any case the ion may arise by a secondary process. The formation of ethyl radicals by pyrolysis on the filament followed by diffusion back into the ionization chamber would lower the observed appearance potential. However, it is difficult to see, in view of the thermal instability of ethyl, why this effect should be larger than for the more stable methyl or allyl radicals.

The appearance potential of the mass 39 ion from propyne was not measured since this ion may arise by two different processes

$$CH:C.CH_3 + e \to CH:C.CH_2^+ + H + 2e$$
<sup>[1]</sup>

$$CH:C.CH_3 + e \to C:C.CH_3^+ + H + 2e$$
[2]

depending on which hydrogen atom is lost. In order to find out the extent to which process [2] occurs, the mass spectrum of a sample of  $CH:C.CD_3$ , kindly prepared by Dr. L. C. Leitch, was examined. The isotopic purity of the sample was determined from the mass spectrum obtained with electrons of energy sufficient to form the molecular ion but insufficient to form dissociation products (25). As shown in Table I, the sample was about 80% CH:C.CD<sub>3</sub>.\* In the 50-volt spectrum, after the parent ions have been subtracted in the

\*The improbable rearrangement product  $CD: C. CD_2H$  was assumed to be absent.

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ratio of their abundance, the fragment ion at mass 42 can arise only by

 $CH:C.CD_3+e \rightarrow C:C.CD_3^++H+2e$ [3] and that at mass 41 mainly by

 $CH:C.CD_3 + e \to CH:C.CD_2^+ + D + 2e$ [4]

with a small contribution from the impurity

$$CH:C.CD_2H + e \to CH:C.CD_2^+ + H + 2e.$$
 [5]

		TAI	BLE I
Mass	SPECTRA	OF	TRIDEUTEROPROPYNE

Mass No.	Peak height at low energy	Mole %	Peak height at 50 ev.	Parent ions	Fragment ions
44	0.2	1.1			
43	15.0	79.4	2015	2015	
42	2.8	14.8	798	376	422
41	0.5	2.7	1482	69	1413
40	0.35	<b>2.0</b>		_	

If the contribution from process [5] is ignored, the ratio H loss/D loss from CH:C.CD<sub>3</sub> is then 422/1413 = 0.30. It is possible, however, to correct for process [5] on the assumption that its probability is one half the sum of the probabilities of process [1] and process [2]. The contribution of process [5] to the mass 41 peak is then  $376 \times \frac{1}{2} \times \text{ratio}$  mass 39/mass 40 in propyne (0.859). The fragment peak at mass 41 resulting from process [4] is then  $1413 - (376 \times \frac{1}{2} \times 0.859) = 1252$ , and the corrected ratio of H loss/D loss is 422/1252 or 0.337. This is almost exactly  $\frac{1}{3}$ , suggesting that after a propyne molecule has been struck by a 50-volt electron, the four hydrogens in the excited ion are equivalent and the loss of a hydrogen atom from either end occurs on a statistical basis. Unfortunately the isotopic purity of the sample was not sufficiently high to give appearance potentials for processes [3] and [4] free from interference.

The same inherent ambiguity exists in the mass 43 peak from propane. It has, however, been reported that this ion is mainly  $s-C_3H_7^+$  (18, 26). In addition, it is possible to say that the process

$$C_{3}H_{8}+e \rightarrow s - C_{3}H_{7}+H+2e \qquad [6]$$

will have a lower appearance potential than the process

$$C_{3}H_{8}+e \rightarrow n-C_{3}H_{7}+H+2e \qquad [7]$$

since (21)  $I(n-C_3H_7) > I(s-C_3H_7)$  and  $D(n-C_3H_7-H) > D(s-C_3H_7-H)$ . In view of these considerations it is very probable that  $A(C_3H_7^+)$  corresponds to process [6] and that the derived dissociation energy can be assigned to the  $s-C_3H_7-H$  bond.



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#### RESULTS AND DISCUSSION

The individual and average values obtained for the ionization potentials of the three radicals are given in Table II, together with some measured and calculated values from the literature. The appearance potentials of the radical ions from the derivatives are given in Table III. The dissociation energies for the radical-atom bonds, derived on the assumption that no kinetic energy term is involved, are also given in Table III for comparison with values from the literature. The limits of error shown should be regarded as limits of precision and not of absolute error.

TABLE II

IONIZATION POTENTIALS OF THE FREE RADICALS ETHYL, ISOPROPYL, AND PROPARGYL

				Ionization p	otential (ev.)	
Radical	Source	Individual values	Average	Literature value	Method	
Ethyl	Mercury diethyl	8.80 8.79 8.76 8.78	8.78±0.05	8.67±0.1	Direct electron impact (7)	
Isopropyl	Azoisopropane	7.91	7 00 10 05	$7.43 \pm 0.1$	$A(s-C_3H_7^+)$ from isoalkanes	(20)
		7.93 7.88 7.90	7.90±0.03	7.73 7.81	Calculated Calculated	(4) (22)
Propargyl	Propargyl iodide	$8.23 \\ 8.23 \\ 8.28$	$8.25 \pm 0.08$			

#### Ethyl

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The average value for the ionization potential of the ethyl radical, 8.78  $\pm 0.05$  ev., agrees with that of  $8.67 \pm 0.1$  ev., measured by Hipple and Stevenson, within the combined limits of error. The appearance potential of  $C_2H_5^+$  from ethane,  $13.05 \pm 0.05$  ev., lies within the estimated limits of error of the three previous measurements. Using the present data for  $I(C_2H_5)$  and  $A(C_2H_5^+)$ ,  $D(C_2H_5^--H) = 4.27 \pm 0.10$  ev. (98.5 $\pm 2.3$  kcal./mole). This result is perhaps just significantly higher than the average value from electron impact data (21), and within the limits set by the photobromination data (1).

As described above, the appearance potentials of the ethyl ion from the halides were anomalously low, and no reliable values for the dissociation energies of the ethyl-halide bonds could be obtained. It would be interesting to study the ionization efficiency curves for the ethyl ion from these compounds using some means of detecting fine structure (3, 17).

#### Isopropyl

The measured ionization potential of the isopropyl radical,  $7.90\pm0.05$  ev., is considerably higher than the  $7.43\pm0.1$  ev. derived from the appearance potentials of s-C<sub>3</sub>H<sub>7</sub><sup>+</sup> in the mass spectra of isoalkanes and from the relevant heats of formation (20). It is, in fact, very close to the  $7.94\pm0.1$  ev. derived in the same way for the *n*-propyl radical (21). As discussed in a previous section, there appeared to be no doubt of the identity of the isopropyl radical on the basis of the dimer formed. Even if some *n*-propyl radicals were initially

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APPEARANCE POTENTIALS AND BOND DISSOCIATION ENERGIES TABLE III

		Appe	earance potential (	ev.)	Bond disso	ciation energy (kœ	al./mole)
Substance	Ion	This work	Literature	Reference	This work	Literature	Reference
Ethane	Ethyl	$13.05 \pm 0.05$	$\begin{array}{c} 12.92\pm0.1\\ 12.81\pm0.2\\ 12.71\pm0.4\end{array}$	(11) (11) (16)	$98.5\pm 2.3$	$98\pm 2$ $96.9\pm 1$	(1) $(21)$
Propane	Isopropyl	$11.66 \pm 0.05$	$\begin{array}{c} 11.67\pm0.1\\ 11.5\pm0.3\\ 11.76\pm0.1 \end{array}$	(24) (11) (16)	$86.7\pm 2.3$	$\smile 89$ $94.3\pm 2$	(19) (21)
Isopropyl iodide	Isopropyl	$9.74 \pm 0.05$		1	$42.4 \pm 2.3$	46	(19)
Isopropyl bromide	Isopropyl	$10.45\pm0.05$	ļ		$58.8\pm 2.3$		
Isopropyl chloride	Isopropyl	$11.08 \pm 0.05$			$73.3 \pm 2.3$	ļ	
Propargyl iodide	Propargyi	$10.23 \pm 0.06$			$45.7 \pm 3.2$	ļ	1
Propargyl bromide	<b>Propargy</b> 1	$10.76 \pm 0.06$	ļ	1	$57.9 \pm 3.2$		I

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formed, they would decompose very rapidly at the temperature of the reactor as was found in the attempt to produce the n-propyl radical. With the present method of plotting the ionization efficiency curves, the measured ionization potential would be high if some contribution to the 50 ev. peak at mass 43 had been neglected in calculating the net radical peak height at 50 ev. A decrease of 10% in the net 50 ev. peak height would lower the ionization potential by only 0.05 ev. The four individual values for  $I(s-C_3H_7)$  given in Table III were obtained in two separate experiments separated by an interval of a few days.

The appearance potential of mass 43 from propane  $(11.66 \pm 0.05 \text{ ev.})$  is in good agreement with previously measured values (11, 16, 24). However the value of  $D(s-C_3H_7-H)$  from the present data

 $A(s-C_3H_7+) - I(s-C_3H_7) = 11.66 - 7.90 = 3.76 \pm 0.10 \text{ ev.},$ 

or  $86.7 \pm 2.3$  kcal./mole, would appear to be considerably too low by comparison with the electron impact average of  $94.3 \pm 2$  kcal. The derived dissociation energies for the isopropyl-halide bonds also appear to be low, although the absence of reliable kinetic data for these bonds makes comparison difficult. The appearance potential data for the isopropyl ion would suggest that the measured ionization potential is too high by about 0.3 ev. It is interesting to note that two values of the ionization potential calculated by Franklin and Field (4) (7.73 ev.) and by Stevenson (22) (7.81 ev.) on the basis of a simplified molecular orbital method, both lie between the presently measured value and the average electron impact value. The calculated value of Franklin and Field, 7.73 ev., was based on  $I(CH_3) = 10.07$  ev. and  $I(C_2H_5) = 8.67$  ev., that of Stevenson on the later value for methyl  $I(CH_3) = 9.96$  ev. and  $I(C_2H_5)$ = 8.67 ev. Using  $I(CH_3) = 9.96$  and  $I(C_2H_5) = 8.78$  as measured in this work, the same calculation of the ionization potential of the isopropyl radical gives 7.97 ev. In view of the assumptions and simplifications necessary in such a calculation, it is doubtful whether this result can be considered as support for the high value for  $I(s-C_3H_7)$  found here. It would appear that further work is necessary to resolve the discrepancy.

#### Propargyl

The ionization potential of the propargyl radical,  $8.25 \pm 0.08$  ev., is only slightly higher than the  $8.16 \pm 0.03$  ev. found for the allyl radical (13). This difference is considerably smaller than that between the ionization potentials of propyne  $(10.43 \pm 0.1 \text{ ev.})$  (6) and propylene (9.84 ev.) (8).

The dissociation energies of the propargyl-halide bonds are not known from other sources for comparison purposes, but the derived values seem rather low in view of the high temperature required to dissociate propargyl iodide.

#### REFERENCES

- ANDERSON, H. C. and VAN ARTSDALEN, E. R. J. Chem. Phys. 12: 479. 1944.
   AUSLOOS, P. and STEACIE, E. W. R. Bull. Soc. chim. Belges, 63: 87. 1954.
   FOX, R. E., HICKAM, W. M., and KJELDAAS, T. Phys. Rev. 89: 555. 1953;  $90 \cdot 386$ 1953.
- FRANKLIN, J. L. Private communication.
- FRASER, R. G. J. and JEWITT, T. N. Proc. Roy. Soc. (London), A, 160: 563. 1937. Phys. Rev. 50: 1091. 1936.

#### FARMER AND LOSSING: FREE RADICALS

- GAUTHIER, F. and PILON, J. R. Unpublished work.
   HIPPLE, J. A. and STEVENSON, D. P. Phys. Rev. 63: 121. 1943.
   HONIG, R. E. J. Chem. Phys. 16: 105. 1948.
   INGOLD, K. U. and LOSSING, F. P. J. Chem. Phys. 21: 1135. 1953.
   IVIN, K. J., WIJNEN, M. H. J., and STEACLE, E. W. R. J. Phys. Chem. 56: 967. 1952.
   KOFFEL, M. B. and LAD, R. A. J. Chem. Phys. 16: 420. 1948.
   LOSSING, F. P., INGOLD, K. U., and HENDERSON, I. H. S. Applied Mass Spectrometry, Institute of Petroleum, London 1954.
   LOSSING, F. P., INGOLD, K. U., and HENDERSON, I. H. S. J. Chem. Phys. 22: 621. 1954.
   LOSSING, F. P., INGOLD, K. U., and TICKNER, A. W. Discussions Faraday Soc. No. 14: 34. 1953
- 1953.

- 1953.
   LOSSING, F. P. and TICKNER, A. W. J. Chem. Phys. 20: 907. 1952.
   MITCHELL, J. J. and COLEMAN, F. F. J. Chem. Phys. 17: 44. 1949.
   MORRISON, J. D. J. Chem. Phys. 19: 1305. 1951.
   SCHISSLER, D. O., THOMPSON, S. O., and TURKEVICH, J. Discussions Faraday Soc. No. 10: 46. 1951.
- 46. 1951.
   STEACIE, E. W. R. Atomic and free radical reactions. Reinhold Publishing Corporation, New York. 1954.
   STEVENSON, D. P. Discussions Faraday Soc. No. 10: 35. 1951.
   STEVENSON, D. P. Trans. Faraday Soc. 49: 867. 1953.
   STEVENSON, D. P. Abstracts A.C.S. Meeting. Kansas City. April 1954.
   STEVENSON, D. P. and HIPPLE, J. A. J. Am. Chem. Soc. 64: 1588. 1942. (Corrected to I(argon) = 15.77 ev.)
   STEVENSON, D. P. and WAGNER, C. D. J. Am. Chem. Soc. 72: 5612. 1950.
   STEVENSON, D. P. and WAGNER, C. D. J. Chem. Phys. 19: 11. 1951.
   SZWARC, M. Discussions Faraday Soc. No. 10: 143. 1951.
   WARREN, J. W. Nature, 165: 810. 1950.