exponent to vary between 2.40 at 570° to 3.8 at 666°, a result similar to those discussed above.

It is significant that the work reported by Hoare and Walsh and by Vanpée and Grard, together with the present work, has been performed in quartz. That the nature of the surface is an important variable in determining the maximum rate has been pointed out by a number of observations (see for example reference 6). Norrish and Foord,[9] working in soda glass, found that the maximum rate corresponded to values of $m = 2$, $x = t = 1$ in the neighborhood of 500°. However, on going to a quartz vessel and a higher temperature (620°), they found an over-all order closer to 3 rather than 4.

The proportionality between the oxygen at the formaldehyde maximum and the initial oxygen illustrates how it may be possible to relate the dependence of a variable such as the rate of reaction at the formaldehyde maximum to the initial oxygen concentration when, strictly speaking, the variable should be related to the oxygen concentration at the maximum. The significance of this observation is still obscure at the present time.

The relationship between the time at which the maximum formaldehyde concentration appears and the oxygen concentration at the maximum is similar to observations that have been reported for other oxidation systems. Chamberlain and Walsh[10] reported the induction period for the oxidation of isopropyl ether to be a linear function of the reciprocal oxygen concentration. The relationship between this observation and the mechanism of reaction is, however, not clear.

The work reported here, along with other recent experiments on methane oxidation, show that no mechanism so far proposed is sufficiently general to cover entirely the slow oxidation of methane. Before better proposals can be made, however, it will be necessary to obtain more experimental data of the type reported here that show detailed relationships between variables of kinetic importance. The variation of the maximum formaldehyde concentration with methane concentration is being investigated along with other factors of significance in order that such relationships can be found. It is believed that when sufficient data are available, explanations can be found for the phenomena observed in methane oxidation.

Acknowledgment.—The author wishes to acknowledge the helpful assistance of Mr. G. C. McCollum in carrying out much of the experimental work reported here.

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[9] R. G. W. Norrish and S. G. Foord, *Proc. Roy. Soc. (London)*, **157A**, 503 (1936).

[10] G. H. N. Chamberlain and A. D. Walsh, *Rev. inst. franç. pétrole*, **4**, 301 (1949).

BAYTOWN, TEXAS

[CONTRIBUTION, ISSUED AS N.R.C. NO. 4964, FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Free Radicals by Mass Spectrometry. XIV. Ionization Potentials of Propyl and Butyl Free Radicals

BY F. P. LOSSING AND J. B. DESOUSA[1]

RECEIVED JUNE 11, 1958

The ionization potentials of *n*-propyl, *n*-, *sec*-, iso-, and *t*-butyl radicals have been measured by electron impact on radicals which were generated thermally by the pyrolysis of appropriate alkyl nitrites, and allowed to flow into the ionization chamber of a mass spectrometer. The ionization potentials were found to be: *n*-propyl 8.69 v., *n*-butyl 8.64 v., isobutyl 8.35 v., *sec*-butyl 7.93 v., and *t*-butyl 7.42 v. Values calculated by a group orbital method are in good agreement with these. The thermal decomposition of the alkyl radicals was found to proceed by a split into a radical (or H atom) and an olefin without intramolecular migration of a hydrogen atom.

Introduction

Some years ago Hipple and Stevenson[2] measured the ionization potentials of the methyl and ethyl radicals by direct electron impact on radicals generated thermally close to the ionization chamber of a mass spectrometer. A number of recent redeterminations of these ionization potentials have been made, and the agreement is, in general, quite good. A spectroscopic measurement of the ionization potential of the methyl radical[3] agrees closely with the electron impact data. Ionization potentials for a number of other radicals have been measured by electron impact and a summary of the values has appeared recently.[4]

With the exception of the *sec*-propyl radical,[5] no direct measurements of the ionization potentials of the higher alkyl radicals have been made. Values have been derived indirectly for the *n*-propyl, *sec*-propyl, *n*-butyl and *t*-butyl radicals[6–8] by combining appearance potentials of propyl and butyl ions with thermochemical data. Some uncertainties arise in the indirect method owing to the difficulty of identifying the structure of the propyl and butyl ions produced in the dissociative ionization processes. The appearance potentials of these ions from normal paraffins, for example, were found to be consistent, not with a primary structure for the ions as might be expected but with the formation of

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[1] National Research Laboratories Post-doctorate Fellow 1955–1957.

[2] J. A. Hipple and D. P. Stevenson, *Phys. Rev.*, **63**, 121 (1943).

[3] G. Herzberg and J. Shoesmith, *Can. J. Phys.*, **34**, 523 (1956).

[4] F. P. Lossing, *Ann. N. Y. Acad. Sci.*, **67**, 499 (1957).

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

[6] D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

[7] D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

[8] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

ions having the secondary configuration.[7] Evidently an isomerization occurred prior to or during the dissociation of the parent ion. On the other hand, there was some evidence that the dissociative ionization of *n*-propyl chloride and *n*-propyl mercaptan yielded the *n*-propyl ion.

As a result of this difficulty, it appeared that more reliable values for the ionization potentials of the propyl and butyl radicals could be had by the direct method, in which radicals of known identity are subjected to electron impact. A knowledge of these ionization potentials is of value, not only for assistance in the interpretation of dissociative ionization processes, but also in the fields of organic reactions and electronic structure.

Experimental

The mass spectrometer[9] and the thermal reactors[5,10] have been described in earlier publications. The "low pressure" reactor, similar to that used by Hipple and Stevenson,[2] consisted of a short length of quartz tubing of 1.5 mm. inside diameter heated by a tantalum furnace element. The reaction products issuing from the reactor at a pressure of about 10^{-3} mm. passed into the ionization chamber through a 2 mm. hole in the top plate. In the "high pressure" reactor, the parent compound was decomposed in a fast flow system using helium as a carrier. A portion of the reaction stream was allowed to pass through a 0.028 mm. orifice in a quartz thimble into the ionization chamber. The conditions under which the decomposition reaction proceeded were quite different in the two reactors. In the "low-pressure" reactor conditions favored the occurrence of wall reactions, and the non-radical products were rather different from those found in the "high pressure" reactor, in which the non-radical products were mainly the result of radical–radical interactions in the gas phase. A comparison of the ionization potential curves obtained for a given radical using the two reactors therefore provided a means of ensuring that the proper corrections for contributions of non-radical species to the peak at the mass of the radical ion had, in fact, been made.

Production of the Radicals.—Owing to the thermal instability of the *n*-propyl and the *n*-, iso- and *sec*-butyl radicals considerable difficulty was encountered in finding a method of producing the radicals in good yield by a pyrolytic reaction. It was found previously that at the temperatures required for essentially complete decomposition of such parent compounds as mercury di-*n*-propyl and azo-*n*-propane, the *n*-propyl radicals were completely dissociated into methyl radicals and ethylene even at the shortest contact times which could be employed.[10] This difficulty was avoided in the present work by making use of the thermal decomposition of the appropriate alkyl nitrites, which proceeded according to the reactions

$$\mathrm{RCH_2ONO} \longrightarrow \mathrm{RCH_2O} + \mathrm{NO} \qquad (1)$$

$$\mathrm{RCH_2O} \longrightarrow \mathrm{R} + \mathrm{CH_2O} \qquad (2)$$

$$\mathrm{R} \longrightarrow \text{olefin} + \text{radical} \qquad (3)$$

The activation energy for reaction 1 is 34–37 kcal.,[11-13] appreciably lower than for the primary bond rupture of the azo- or mercury alkyls. The RCH_2O radicals are quite unstable thermally; for instance $D(n\text{-}C_3H_7-CH_2O)$ is approximately 11 kcal./mole.[14] E_3 depends on the identity of R, being of the order of 25 kcal./mole for n-C_3H_7, *n*-, *sec*- and iso-C_4H_9, and about 45 kcal./mole for t-C_4H_9. The rates of the first two reactions might therefore be expected to be of the relative magnitude $k_2 >> k_1$. Reaction 3 would be somewhat faster than (1) for all the radicals except *t*-butyl, but nevertheless conditions would appear favorable for production of the radicals in appreciable quantities.

The thermal decomposition of *n*-butyl nitrite in the "low pressure" reactor was investigated, using ionizing electrons of low energy to simplify the mass spectra of the reactants and products and to enable free radicals to be detected and identified as to mass number. At 350° the nitrite was partially decomposed, and the mass 30 peak, presumably NO, increased greatly. The mass 73 peak increased slightly but decreased rapidly with higher temperature. The mass 43 peak, corresponding to the *n*-propyl radical, increased considerably with temperature, reaching a maximum at about 475°. Above 525° the 43 peak decreased with temperature and was replaced by peaks at mass 28 and mass 15. The latter evidently were the parent peaks of ethylene and methyl radicals resulting from the thermal decomposition of the *n*-propyl radical. An identification of the transient species at mass 73 was less unambiguous since this mass corresponds not only to the n-C_4H_9O radical but to the addition product of *n*-propyl and NO. If it were the latter, the maximum peak height would be expected to occur at a temperature at which the *n*-propyl radical was most abundant, rather than at 350–400°. It seems quite likely, therefore, that the mass 73 peak corresponds to the butyloxy radical, n-C_4H_9O. Its disappearance above 400°, at which temperature the *n* propyl radical became an important product, is consistent with this interpretation.

The sequence of reactions for the other nitrites was also in agreement with reactions 1, 2 and 3 above, although in the case of 2-methylbutyl nitrite and neopentyl nitrite, the corresponding branched amyloxy radicals could not be detected. The products of decomposition of the radicals are discussed in a later paragraph. A small amount of side reaction to form the alcohol RCH_2OH and aldehyde RCHO was observed, possibly as a result of the disproportionation of the alkoxy radicals on the walls of the reactor.

Preparation of Alkyl Nitrites.—The nitrites were prepared from the appropriate alcohols by reaction with sodium nitrite and dilute sulfuric acid.[15] The nitrites were separated, washed with aqueous sodium bisulfite and bicarbonate, dried over anhydrous sodium sulfate and fractionally distilled at reduced pressure. In most cases the mass spectra showed the presence of traces of the alcohol RCH_2OH and aldehyde RCHO. Since these were also by-products of the thermal decomposition, their presence did not interfere seriously.

Measurement of the Ionization Potentials.—The method of obtaining the ionization efficiency curves of the radical ion and of the added standard gas, usually krypton or xenon, has been described.[16] The net peak height for the radical at mass R, using 50 volt electrons, was determined from the total peak by subtracting the contributions from undissociated RCH_2ONO, from the dimer RR and from the by-products RCH_2OH and RCHO. The ratio of the R^+ peak to the parent peak for these compounds was measured in separate experiments using the pure compound where possible. In some cases the aldehydes were not available, and the ratios were taken from the literature.[17] The net radical peak remaining after all contributions had been removed accounted for 0.3 to 0.5 of the total R^+ peak. No difficulty was encountered in obtaining a net peak height of 100 to 200 cm. (2-4×10^{-12} amp.) for the radical itself.

The logarithm of the ratio of the peak height at a given electron accelerating potential to the net peak height at 50 v. was plotted against the electron accelerating potential. A set of ionization efficiency curves for the isobutyl radical and for the standard, in this case xenon, is shown in Fig. 1. In the region from 1 to 0.1% the two curves are parallel within 0.02 v. This observation is in agreement with earlier evidence that such curves for parent ions are almost invariably parallel within 0.05 v. over this range when plotted as a per cent. of the 50 v. peak, provided that the 50 v. peaks are not greatly different in height.

As a check on the instrumental factors involved in the measurement of the ionization efficiency curves, the ionization potential of isobutyl radical was determined using two mass spectrometers, one fitted with a "low pressure" reactor, the other with a "high pressure" reactor. The average

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(9) F. P. Lossing, K. U. Ingold and A. W. Tickner, *Disc. Faraday Soc.*, **14**, 34 (1953).

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

(11) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1954.

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

(13) M. F. Nagiew, Z. G. Petrova and A. I. Sultanova, *Doklady Akad. Nauk, S.S.S.R.*, **109**, 573 (1956).

(14) P. Gray, "Fifth Symposium on Combustion," Reinhold Publ. Corp., New York, N. Y., 1955, p. 535.

(15) "Organic Syntheses," Vol. XVI, John Wiley and Sons, Inc., New York, N. Y., 1936.

(16) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

(17) J. A. Gilpin and F. W. McLafferty, *Anal. Chem.*, **29**, 990 (1957).

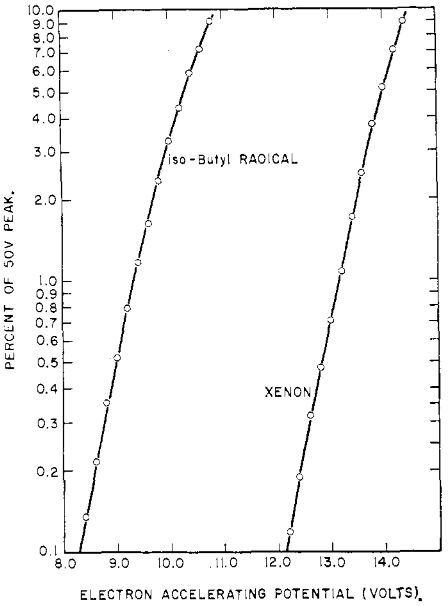

Fig. 1.—Ionization efficiency curves for isobutyl radical and xenon standard.

values obtained were 8.32 ± 0.05 and 8.38 ± 0.05 v. These are in good agreement, in spite of the fact that the proportions of non-radical products were quite different in the two cases. This shows that the errors arising from the compound nature of the radical peak were negligibly small after the corrections had been applied. It also shows that the observed ionization potential could be reproduced on a different instrument.

Results and Discussion

The values obtained for the vertical ionization potentials of the five radicals are given in Table I. The ionization potential of the *sec*-propyl radical, measured previously,[5] is also included. The limits of error given in the table represent the average deviation from the mean of three or more determinations and should not be considered an estimate of the absolute error. The ionization potentials obtained are, in most cases, significantly higher than those obtained from appearance potentials by the indirect method, which are given in Table **I** for comparison.

TABLE I

IONIZATION POTENTIALS OF PROPYL AND BUTYL RADICALS

Radical	Directly measured I.P.	Indirectly measured I.P.	
n-C_3H_7	8.69 ± 0.05	7.94[7]	8.33[8]
sec-C_3H_7	7.90 ± .05[5]	7.43[6]	
n-C_4H_9	8.64 ± .05	8.3[8]	
iso-C_4H_9	8.35 ± .05	..	
sec-C_4H_9	7.93 ± .05	8.0[8]	
t-C_4H_9	7.42 ± .07	6.90[6]	

Ionization potentials measured by electron impact are generally considered to represent "vertical" transitions in the Franck–Condon sense, and therefore it is expected that they will be slightly larger than the "adiabatic" values. The magnitude of the difference is found to be about 0.1 v. for olefins but can amount to several tenths of a volt for aromatic compounds. Since no adiabatic values are available for paraffins, an estimate of the difference cannot be made. It is difficult to say how large a difference might be expected for an alkyl free radical, although it may be noted that the average of a number of measurements of $I(CH_3)$ by electron impact is greater than the spectroscopically determined value[3] by less than 0.1 v.

The change in the vertical ionization potential of the alkyl radicals with structure is quite systematic, as can be seen by reference to Fig. 2, in which the values, including those of methyl,[16] ethyl[5] and *sec*-propyl[5] radicals, have been plotted against carbon number. Repeated substitution, by CH_3 groups, of H-atoms on the carbon carrying the free electron results in a large decrease in ionization potential as shown by the series: methyl, ethyl, *sec*-propyl and *t*-butyl. A decrease of about the same size occurs on going from *n*-propyl to *sec*-butyl, in which the substitution is also on the carbon having the free electron. On the other hand, a CH_3 substitution on carbons α and β to the free electron brings about only a slight decrease in ionization potential, as shown by the series: ethyl, *n*-propyl and *n*-butyl. The apparent slight reversal of this trend in the case of *sec*-propyl and *sec*-butyl is without significance since the difference, 0.03 v., is considerably smaller than the combined limits of error.

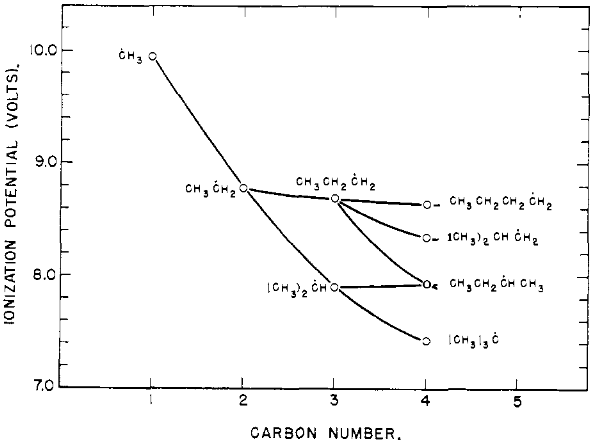

Fig. 2.—Changes in ionization potential with substitution by methyl groups.

It is apparent from these curves that the decrease of 0.31 v. found between *n*-propyl and isobutyl is surprisingly large. Since the substitution is at the carbon adjacent to the free electron, the decrease would be expected to be about the same as between ethyl and *n*-propyl, that is, about 0.1 v. As mentioned above, the value for $I(iso\text{-}C_4H_9)$ was remeasured under rather different conditions using a second mass spectrometer. From the good agreement obtained it appears that this result is not low as a result of experimental error.

Calculation of Ionization Potentials—A semi-empirical method of calculating ionization potentials in a homologous series recently has been developed by Hall[18] and Lennard-Jones and Hall.[19] A simplified method, in which group orbitals were

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[18] G. Hall, *Proc. Roy. Soc.* (*London*), **A205**, 541 (1951).

[19] J. Lennard-Jones and G. G. Hall, *Disc. Faraday Soc.*, **10**, 18 (1951).

employed,[20] was used successfully by Hall to calculate ionization potentials for a number of hydrocarbons[21] and by Franklin for hydrocarbon derivatives and a number of other types of compound.[22] Using this method, Stevenson[23] calculated ionization potentials for the propyl and butyl radicals. The values were not generally in agreement with the indirectly determined ionization potentials, but, as can be seen from Table II, they are in quite good agreement with the directly determined values reported here.

TABLE II

CALCULATED AND MEASURED IONIZATION POTENTIALS

	Calcd.		
	Stevenson[23]	This work	Measured
CH_4	(13.04)	(13.12)	
C_2H_6	(11.76)	(11.76)	
CH_3	(9.96)	(9.95)	
C_2H_5	(8.67)	(8.78)	
b	1.28	1.36	
c	2.37	2.253	
n-C_3H_7	8.58	8.68	8.69
sec-C_3H_7	7.81	7.97	7.90
n-C_4H_9	8.57	8.64	8.64
iso-C_4H_9	8.42	8.55	8.35
sec-C_4H_9	7.76	7.87	7.93
t-C_4H_9	7.11	7.32	7.42
Propane	11.23	11.19	11.21[24]
n-Butane	10.97	10.65	10.80[24]

The calculation, as applied to the alkyl free radicals, requires four parameters: (1) the potential parameter for a saturated alkane or alkyl CH_3 group, taken as the ionization potential of methane, (2) a saturate–saturate interaction, here designated as b, which is taken as the difference $I(CH_4) - I(C_2H_6)$, (3) the parameter associated with a free CH_3 group, taken as $I(CH_3)$, and (4) a saturate–unsaturate interaction, here designated as c, evaluated from the ionization potential of C_2H_5 radical using the determinant

$$\begin{vmatrix} e - E & c \\ c & - E \end{vmatrix} = 0$$

In this expression e is $I(CH_4)$, f is $I(CH_3)$ and E is $I(C_2H_5)$. According to this formulation, the determinant for the *sec*-butyl radical $CH_3CH_2CHCH_3$ has the form

$$\begin{vmatrix} e - E & b & & \\ b & e - E & c & \\ & c & f - E & c \\ & & c & e - E \end{vmatrix} = 0$$

The lowest root gives the ionization potential of the *sec*-butyl radical.

The calculated ionization potentials are not particularly sensitive to small variations in the values chosen for the four parameters. As an example, in Table II there is given a set calculated using $I(CH_4) = 13.12$ v., which is the average of a large number of determinations,[8] $I(C_2H_6) = 11.76$ v.,[24] $I(CH_3) = 9.95$ v.[16] and $I(C_2H_5) = 8.78$ v.[5] The individual values differ only slightly from those calculated by Stevenson, but the over-all agreement with the experimental values is slightly better. The ionization potentials of propane and n-butane have also been calculated using both sets of parameters, and in both cases the agreement with the measured values[24] is satisfactory. It is remarkable that a calculation based on such a simple model is capable of reproducing the experimental values so closely. The largest discrepancy (0.2 v.) occurs in the value for isobutyl, for which the experimental result, as discussed above, seems to be unexpectedly low. The simplified calculation used here is based on the assumption of planarity of the molecule and ion, and it is perhaps significant that of the four butyl ions, the only one which cannot have a planar configuration is the isobutyl ion.

Appearance Potentials and Bond Dissociation Energies.—In Table I are given a number of values for the ionization potentials derived from a combination of appearance potential and thermochemical data by Stevenson[6,7] and from D'Or and Collin's data[25] as calculated by Field and Franklin.[8] In one case, that of *sec*-C_4H_9 radical, the agreement is quite good, but for the other radicals the indirect values are appreciably lower than the directly measured ones.

One possible cause of the discrepancies observed is the uncertainty involved in placing the appearance potential of a molecular or fragment ion on an absolute energy scale. For molecular ions and some fragment ions, the ionization efficiency curves when suitably normalized are found to have essentially the same shape as the curves for a rare gas standard (see Fig. 1). For such ions, any one of the methods in current use for comparison of the curves with that of a standard gas will give approximately the same value for the appearance potential. On the other hand, some fragment ions exhibit ionization efficiency curves which rise much more gradually at the threshold. In such cases the observed appearance potential will depend to a considerable extent on the method of evaluation and on the sensitivity of detection. For the determination of bond dissociation energies from appearance potentials by the indirect method, energy differences only are required,[6,7] and these are determined under conditions of identical sensitivity on a single mass spectrometer. It is possible therefore for such energy differences, and the values for bond dissociation energies derived therefrom, to be valid although the appearance potentials are not on an absolute energy scale. On the other hand, when these appearance potentials are used to derive ionization potentials for radicals, the question of the energy scale becomes important.

A further question arises as to whether the ionic species formed by the ionization of a radical is the same as that formed in the dissociative ionization of a derivative of the radical. In the dissociative ionization of n-alkanes, for example, the probability of an isomerization to form *sec*-$C_3H_7^+$ ions was pointed out by Stevenson.[7] A summary of the electron impact data for n-C_3H_7 and *sec*-C_3H_7 com-

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[20] J. Lennard-Jones and G. G. Hall, *Proc. Roy. Soc.* (*London*), **A213**, 102 (1952).

[21] G. G. Hall, *Trans. Faraday Soc.*, **49**, 113 (1953); **50**, 319 (1954).

[22] J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).

[23] D. P. Stevenson, Preprint No. 29, Symposium on Mechanics of Homogeneous and Heterogeneous Hydrocarbon Reactions, ACS Meeting, Kansas City, March, 1954.

[24] R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

[25] L. D'Or and J. Collin, *Bull. soc. roy. sci. Liege*, **22**, 285 (1953).

pounds given by Franklin and Field[8] in the form of values of ΔH_f for propyl ions shows that all but two of the values lie in the range 188–195 kcal./mole regardless of whether the ions were formed from *n*-C_3H_7 or *sec*-C_3H_7 derivatives. These data suggest further that only one species of $C_3H_7^+$ ion is formed in these dissociative ionization processes. On the basis of the ionization potentials of *n*- and *sec*-propyl radicals measured in this work, it seems clear that a heat of formation of 188–195 kcal./mole is much too low to correspond to a *n*-$C_3H_7^+$ ion. On the assumption that this is the *sec*-$C_3H_7^+$ ion, taking an average gives $\Delta H(sec\text{-}C_3H_7^+) = 193$ kcal./mole. Using $I(sec\text{-}C_3H_7) = 7.90$ v. (182 kcal./mole), then $\Delta H_f\ (sec\text{-}C_3H_7)$ would be 11 kcal./mole. Since $\Delta H_f(C_3H_8) = -24.8$ kcal./mole[26] and $\Delta H_f(H) = 52.1$ kcal./mole,[27] one is led to a value of $D(sec\text{-}C_3H_7\text{—}H) = 88$ kcal./mole. This result is about 6 kcal./mole lower than the indirect electron impact value.[6] It should be emphasized that owing to the uncertainty as to the identity and heat of formation of the $C_3H_7^+$ ion formed in the dissociative ionization processes, the 88 kcal./mole value derived above should be considered as having no validity whatever and is cited only to illustrate the difficulties encountered in the interpretation of the data.

The available appearance potential data for butyl ions also have been summarized and recalculated as ionic heats of formation by Field and Franklin.[8] These values range from 165 kcal./mole to about 200 kcal./mole. Although the butyl ions from *t*-butyl derivatives tend, on the average, to have lower heats of formation than those from derivatives of the other butyl radicals, they are by no means consistent in this respect. In other compounds it is also not evident which butyl ion may be formed. In such circumstances it is apparent that values for bond dissociation energies derived using the $A(R^+) - I(R)$ relation, and the existing appearance potential data would be quite unreliable.

Thermal Decomposition of Propyl and Butyl Radicals.—Very little information is available from the literature on the modes of dissociation of the isomeric propyl and butyl radicals. As pointed out by Trotman-Dickenson,[28] even when rates of decomposition for propyl and butyl radicals have been measured, it is in most instances not known which of the isomeric radical species was involved. If the products of decomposition of each radical species were known, the identification would be greatly facilitated.

In the present work some qualitative observations on the modes of decomposition of the *n*-propyl and the four butyl radicals have been made. Using low energy electrons to identify the products, reactions (4) to (8) were found to occur

$$CH_3CH_2\dot{C}H_2 \longrightarrow CH_3 + C_2H_4 \tag{4}$$

$$CH_3CH_2CH_2\dot{C}H_2 \longrightarrow C_2H_5 + C_2H_4 \tag{5}$$

$$(CH_3)_2CH\dot{C}H_2 \longrightarrow CH_3 + C_3H_6 \tag{6}$$

$$CH_3CH_2\dot{C}HCH_3 \longrightarrow CH_3 + C_3H_6 \tag{7}$$

$$(CH_3)_3\dot{C} \longrightarrow H + (CH_3)_2C{:}CH_2 \tag{8}$$

The sensitivity for detection using this method was rather low, and it is estimated that an alternative dissociation amounting to 5% of the total would not have been detected. Within this limit, however, only one mode of dissociation was observed for each of the radicals, as given above. None of the radicals decomposed by way of a hydrogen migration. Reactions 5 and 7 are in agreement with the conclusions of McNesby, Drew and Gordon[29] that intramolecular hydrogen shifts do not occur in the thermal decomposition of the *n*-butyl and *sec*-butyl radicals. It is interesting to note that the decomposition of the *t*-butyl radical proceeds by a C–H split, even though an alternative mode of dissociation into CH_3 and C_3H_6 by way of an intramolecular H atom shift is less endothermic by about 11 kcal./mole.

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[26] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

[27] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," N.B.S. Circular 500 (1952).

[28] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955.

[29] J. R. McNesby, C. M. Drew and A. S. Gordon, *J. Chem. Phys.*, **24**, 1260 (1956).

ONTARIO, CANADA

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Molecular Structure of Carbon Suboxide[1]

BY R. L. LIVINGSTON AND C. N. RAMACHANDRA RAO[2]

RECEIVED JUNE 2, 1958

The molecular structure of carbon suboxide has been studied by electron diffraction by the visual interpretation of sectored plates. The bond distances obtained were C–C = 1.28 ± 0.01_5 Å. and C–O = 1.16 ± 0.01_5 Å. The diffraction data are consistent with a linear symmetric structure but small deviations from linearity cannot be excluded.

Introduction

Previous electron diffraction investigations[3–5] of the molecular structure of carbon suboxide employed the visual method with non-sectored plates and hence did not yield highly accurate interatomic

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[1] Contains material from the Ph.D. thesis of C. N. Ramachandra Rao.

[2] Purdue Research Foundation Fellow, 1956–1957; Standard Oil Foundation Fellow, 1957–1958.

[3] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933).

[4] H. Boersch, *Monatsh.*, **65**, 311 (1935).

[5] H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 937 (1951).