

[CONTRIBUTION FROM WESTINGHOUSE RESEARCH LABORATORIES]

Ionization and Dissociation by Electron Impact: Isobutylene, Propane, and PropyleneBY D. P. STEVENSON¹ AND JOHN A. HIPPLE

In a recent paper the results of a mass-spectroscopic investigation of the dissociation products of normal and isobutane were reported.² We present here the results of a similar investigation of isobutylene. As a part of an extensive study of the form of ionization efficiency curves, we have examined certain processes in propane and propylene. Inasmuch as our results on these latter molecules differ from those of a previous investigation, we also report appearance potentials of some of the ions in the mass spectra of propane and propylene.

The instrument and general technique have been described in the preceding article.² The gas samples were given to us by the Standard Oil Company of Indiana.

The appearance potentials, determined from the "initial breaks,"² are summarized in Table I. The results of Delfosse and Bleakney³ on propane and propylene are included for comparison. We can offer no explanation for the discrepancies between our results and those of Delfosse and Bleakney. Careful checks show the results we report are consistent with our previously reported work on ethane and the butanes.

The significance of the appearance potentials of the various ions in the spectra of propylene and propane has been discussed by Delfosse and Bleakney.³ Our values are not sufficiently different to change their interpretation in any significant detail.

The value of the appearance potential of the parent ion in the isobutylene spectrum, $A(C_4H_8^+) = 8.9$ e. v., which is to be associated with $I_{\text{vert}}(i-C_4H_8)$ is surprisingly low. The substitution of two methyl groups in ethylene reduces $I_{\text{vert}}(\pi + \pi_u)$ by ~ 2.0 e. v. The effect of methyl for hydrogen substitution is more marked in the ethylene series than in the corresponding ethane series, since $I_{\text{vert}}(C_2H_6) = 11.7$ e. v. and $I_{\text{vert}}(C_4H_{10}) = 10.4$ e. v.² The $I_{\text{vert}}(\text{ethylenes})$ decrease more or less smoothly with methyl substitution, while the ethane series shows a greater decrease from propane to butane than from ethane to propane.

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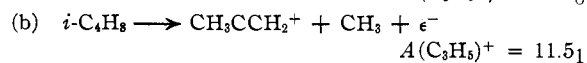
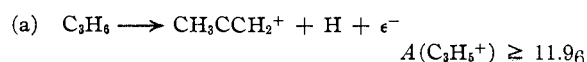
(2) D. P. Stevenson and J. A. Hipple, *THIS JOURNAL*, **64**, 1588 (1942).

(3) J. Delfosse and W. Bleakney, *Phys. Rev.*, **56**, 256 (1939).

It will be noted that while in the ethylene series there is a difference of over 2.2 volts between the appearance potentials of $R-H^+$ and $R^+ + H$, the difference is less than 1.2 e. v. for the saturated hydrocarbons. A similar situation obtains when one compares the appearance potentials of $R-CH_3^+$ and $R^+ + CH_3$ for R olefin or saturate. These observations are consistent with the assumption which is usually made with respect to the relative strengths of single bonds to unsaturated and saturated carbon atoms.⁴

The ionization efficiency curve for $C_4H_8^+$ from isobutylene shows inflections at ~ 12.5 e. v. and at ~ 18 e. v. The inflection at 12.5 probably is to be attributed to the removal of the electron from a C-H bond orbital instead of from a C-C double bond orbital. Although we can make no assignment of the higher ionization potential (~ 18 e. v.), it should be remarked that isobutane also has an ionization potential about 9 volts above the appearance potential. The ionization efficiency curves for $C_4H_8^+$ from $i-C_4H_8$ and for $C_4H_{10}^+$ from $i-C_4H_{10}$ are shown in Fig. 1.

Barring molecular rearrangement, the ion $C_3H_5^+$ formed from isobutylene has the structure $CH_3CCH_2^+$. One might expect the $C_3H_5^+$ formed from propylene to be the isomeric $CH_2CHCH_2^+$ since the bonds to carbon atoms attached to unsaturated carbon atoms are generally weaker (more reactive) than the bonds to an unsaturated atom. The fact that $A(C_3H_5^+)$ from C_3H_6 is 2.2 e. v. greater than $A(C_3H_6^+)$ while $A(C_3H_7^+)$ from C_3H_8 is but 0.5 e. v. greater than $A(C_3H_8^+)$ suggests that the hydrogen atom lost by propylene was attached to one of the ethylenic carbon atoms. In either case we can write



These equations lead to $D(CH_3-H) \leq 4.48$ e. v. This is in good agreement with the value of 4.38 e. v. deduced from other data.⁶ This agreement

(4) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935, p. 75.

(5) F. D. Rossini, *Chem. Rev.*, **27**, 1 (1941), 1 kcal./mole = 0.04337 e. v.

(6) D. P. Stevenson, *J. Chem. Phys.*, **10**, 291 (1942).

TABLE I
APPEARANCE POTENTIALS OF VARIOUS IONS IN C_3H_6 , C_3H_8 , AND IN C_4H_8

Process	$A(X^+)$, e. v. ^a	$A(X^+)$, e. v. ^b
$C_3H_6 \rightarrow C_3H_6^+ + e^-$	9.76 ± 0.1	10.0 ± 0.2
$C_3H_6 \rightarrow C_3H_5^+ + H + e^-$	$11.96 \pm .1$	$11.8 \pm .2$
$C_3H_8 \rightarrow C_3H_8^+ + e^-$	$11.21 \pm .1$	$11.3 \pm .2$
$C_3H_8 \rightarrow C_3H_7^+ + e^-$	$11.67 \pm .1$	$11.9 \pm .2$
$C_3H_8 \rightarrow C_2H_5^+ + CH_3 + e^-$	$12.21 \pm .1$	$12.3 \pm .2$
$C_3H_8 \rightarrow C_2H_4^+ + CH_4 + e^-$	$11.81 \pm .1$	$12.2 \pm .2$
$C_3H_8 \rightarrow CH_3^+ + \dots + e^-$	17 ± 2	...
$i-C_4H_8 \rightarrow C_4H_8^+ + e^-$	$8.86 \pm 0.1; 12.5 \pm 1$	
$i-C_4H_8 \rightarrow C_4H_7^+ + H + e^-$	$11.32 \pm .1$	
$i-C_4H_8 \rightarrow C_3H_5^+ + CH_3 + e^-$	$11.51 \pm .1$	
$i-C_4H_8 \rightarrow C_3H_4^+ + CH_4 + e^-$	$11.62 \pm .1$	
$i-C_4H_8 \rightarrow C_3H_3^+ + \dots + e^-$	$14.2 \pm .5$	
$i-C_4H_8 \rightarrow C_2H_5^+ + \dots + e^-$	15 ± 1	
$i-C_4H_8 \rightarrow C_2H_4^+ + C_2H_4 + e^-$	12.1 ± 0.5	
$i-C_4H_8 \rightarrow C_2H_3^+ + C_2H_4 + H + e^-$	$15.2 \pm .5$	

^a The ionization potential of argon, $I = 15.76$ e. v., was taken in accordance with the new conversion factor, $1 \text{ e. v.} = 8066 \text{ cm.}^{-1}$. The appearance potentials in reference 2 should all be raised 0.07 e. v. We should like to thank the referee who called attention to the inconsistency on this point which existed in our original manuscript. ^b Ref. 3 of text.

suggests either that the unsymmetrical structure for the $C_3H_5^+$ from C_3H_6 is correct or that the isomerization energy of the reaction $CH_2CHCH_2^+ \rightarrow CH_3CCH_2^+$ is quite small. The latter seems very likely, since the allene \rightarrow methylacetylene reaction involves but -0.07 e. v.

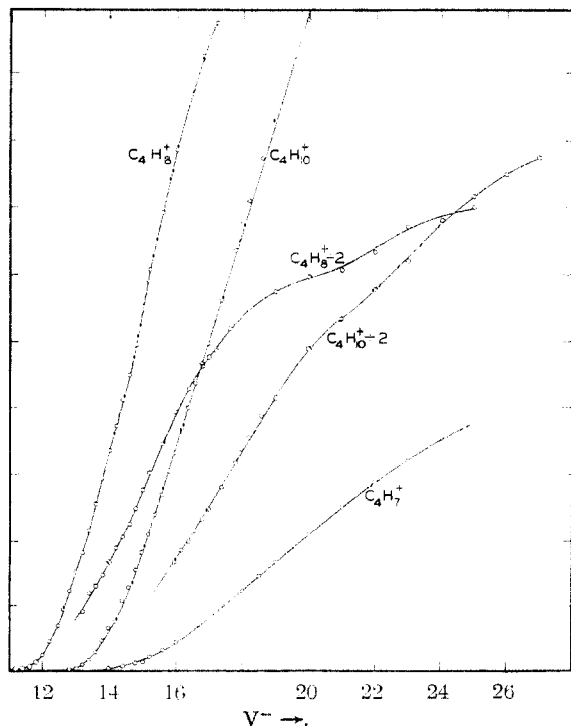


Fig. 1.—Ionization efficiency curves for the reactions $i-C_4H_8 \rightarrow C_4H_8^+$; $i-C_4H_8 \rightarrow C_4H_7^+ + H$; $i-C_4H_{10} \rightarrow C_4H_{10}^+$. The voltage scale is uncorrected. The ordinates for isobutylene and isobutane are not comparable.

The $C_3H_4^+$ from isobutylene may have either the allene or the methylacetylene structure. From the data summarized by Rossini,⁵ we can write

(d) $i-C_4H_8 = CH_2CCH_2 + CH_4$ $\Delta H_{298.1}^\circ = 1.36$ e. v. or

(d') $i-C_4H_8 = CH_3CCH + CH_4$ $\Delta H_{298.1}^\circ = 1.29$ e. v.

Subtracting from $i-C_4H_8$; $A(C_3H_4^+) = 11.62$, we have either $I(CH_2CCH_2) = 10.26$ or $I(CH_3CCH) = 10.33$ e. v. Delfosse and Bleakney³ found from direct measurement on allene, $A(C_3H_4^+) = 9.9$ e. v. The ionization potential of methylacetylene has not been measured. In acetylene, $A(C_2H_2^+) = 11.2$ e. v.⁷ By analogy with the observed decreases in the vertical ionization potential brought about by substituting a methyl group into ethane and ethylene, one may guess that $I_{\text{vert}}(CH_3CCH)$ is 1 e. v. less than $I_{\text{vert}}(C_2H_2)$ or $I_{\text{vert}}(CH_3CCH) = 10.2$ e. v. Thus we are unable to reach a decision with regard to the structure of the $C_3H_4^+$ in the isobutylene spectrum. It may be noted that regardless of the structure of this ion, the methyl and hydrogen which form the methane come from adjacent carbon atoms rather than from the same atom.⁸

The relatively low values of the appearance potentials of the ions $C_2H_5^+$ and $C_2H_4^+$ in the isobutylene spectrum indicate that a minimum number of bonds are lost in the course of the rearrangement and dissociation reactions through which they are formed. The essential sharpness

(7) J. T. Tate, P. T. Smith and A. L. Vaughan, *Phys. Rev.*, **48**, 525 (1935).

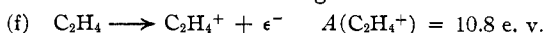
(8) See the discussion in refs. 2 and 3.

with which the ionization efficiency curves (see Fig. 2) rise to their maximum values suggests that but one process is involved in each case, *i. e.*, one set of products. The low precision of $A(\text{C}_2\text{H}_5^+)$ precludes the unique assignment of the un-ionized fragments which accompany the formation of C_2H_5^+ .

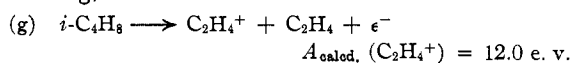
From the data of Rossini⁵ we can write



while Tate and co-workers⁹ give

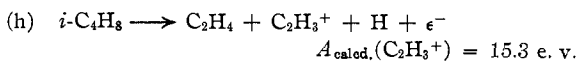


Adding, we find

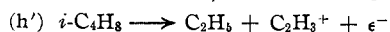


in excellent agreement with the observed value (Table I). If, instead of the electron impact value of $A(\text{C}_2\text{H}_4^+)$, we had used Price's¹⁰ spectroscopically determined $I^\circ(\text{C}_2\text{H}_4) = 10.4 \text{ e. v.}$, the value of $A(\text{C}_2\text{H}_4^+)$ calculated for (g) would be 0.4 e. v. below the observed value. This suggests 0.4 e. v. as a limit to the activation energy of the reverse of reaction (g). We have assumed that the products are of the ethylene rather than the ethylidene structure, an assumption which is unwarranted at present. Until the energies of ethylidene and its ion are known from other data, this ambiguity in the foregoing discussion must remain unresolved.

The ionization efficiency curve of the ion of mass 27 (primarily C_2H_3^+) of the isobutylene spectrum is similar in form to the curves for this ion in the spectra of ethane and the butanes. The rather large range of electron energies through which the slope increases suggests that one or more secondary processes, involving more fragmentation than the primary process, are involved. Combining reaction (e) with C_2H_4 , $A(\text{C}_2\text{H}_3^+) = 14.1 \text{ e. v.}$,⁹ we find



in good agreement with the observed value of $A(\text{C}_2\text{H}_3^+) = 15.2 \text{ e. v.}$ We cannot exclude C_2H_5 as the un-ionized product which accompanies the C_2H_3^+ . The association of C_2H_4 and H to C_2H_5 gives off about 1.7 e. v., thus for the reaction



one would estimate $A(\text{C}_2\text{H}_3^+) \cong 13.6 \text{ e. v.}$, well below the observed value. The 1.5 e. v. discrepancy could easily be assigned to an activation energy of the reverse of reaction (h').

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

(10) W. C. Price, *ibid.*, **47**, 444 (1935).

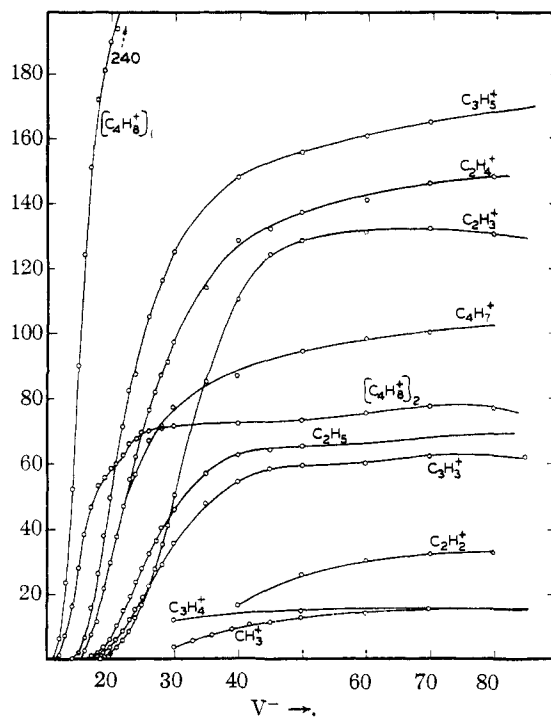
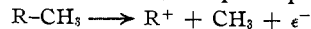


Fig. 2.—Ionization efficiency curves for various processes in isobutylene. $(\text{C}_4\text{H}_8^+)_1$ is to be compared with the C_2 masses. $(\text{C}_4\text{H}_8^+)_2$ is to be compared with the C_3 masses.

The form of the ionization efficiency curve of CH_3^+ from propane is of a character intermediate to those of this ion in ethane and the butanes. The formation of the methyl ion in the ethane spectrum involves mainly single ionization and in the butanes only double ionization. The value of $A(\text{CH}_3^+)$ from propane, while only rough, indicates that a process involving only single ionization contributes. The very pronounced curvature of the ionization efficiency curve in the vicinity of 26 volts indicates double ionization to be the more important source of methyl ions. The CH_3^+ current from propane attains about 10% of its maximum value for 30 volt electrons, while for similar electrons in ethane, CH_3^+ is 50% of its maximum value. The methyl ion current is but 6% of its maximum value for 30 volt electrons in the butanes.

The relative abundances of the various ions in the mass spectrum of isobutylene are given, for round values of the bombarding electron energy in Table II. Qualitatively, the distribution of intensities is very like that observed in the butane spectra. As is the case in the spectra of propylene, propane and the butanes, the principal reaction is



In the C_4 region of the spectrum, isobutylene

TABLE II
 THE MASS SPECTRUM OF ISOBUTYLENE^a

$m/e =$	56	55	54	53	52	51	50	49	48	
$V^-_{ion} =$	$C_3H_8^+$	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$	$C_3H_2^+$	C_3H^+	C_2^+	
30	100	33.3	3.9	
50	103	40.8	4.9	11.0	2.5	8.6	8.4	1.6	0.22	
70	108	43.6	4.8	10.8	2.3	8.5	9.7	2.6	.38	
100	107	45.1	5.2	11.2	2.2	8.3	10.3	3.2	.54	
$m/e =$	42	41	40	39	38	37	36			
$V^-_{ion} =$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$	$C_3H_2^+$	$C_3H_2^+$	C_3H^+	C_3^+			
30	16.1	175	16.9	50.1			
50	18.2	218	21.4	83.8	11.3	5.1	0.25			
70	18.7	231	22.4	87.4	12.7	7.5	.88			
100	17.2	243	22.6	87.0	12.7	8.1	1.33			
$m/e =$	29	28	27	26.5	26	25.5	25	24	15	14
$V^-_{ion} =$	$C_2H_5^+$	$C_2H_4^+$	$C_2H_3^+$	$C_2H_2^+$	$C_2H_2^+$	$C_2H_3^{++}$	C_2H^+	C_2^+	CH_3^+	CH_2^+
30	18.8	42.2	21.4	1.4	0.09
50	28.1	59.5	55.1	..	11.0	0.5	5.5	1.9
70	29.1	63.3	56.6	..	13.9	6.5	..
90	29.9	64.8	55.7	0.22	14.3	2.8	2.3	0.25	6.7	..

^a No correction for C^{13} in its natural abundance, 1.1%.

shows its generic relationship to isobutane. The manner in which the spectrum changes with electron energy is illustrated in Fig. 2.

Summary

The results of a mass-spectroscopic investigation of the ionization and dissociation of propylene, propane and isobutylene by electron impact

are reported. The vertical ionization potentials of these three molecules were found to be $I_v(C_3H_6) = 9.8 \pm 0.1$ e. v., $I_v(C_3H_8) = 11.2 \pm 0.1$ e. v., and $I_v(i-C_4H_8) = 8.9 \pm 0.1$ e. v. The significance of some of the observed appearance potentials of ions in the isobutylene spectrum is discussed. The mass spectrum of isobutylene is given in detail.

EAST PITTSBURGH, PA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Reactions of Cobalt(III), Cobalt(II), and Iron(II) Oxides in Liquid Ammonia

BY THOMAS E. MOORE AND GEORGE W. WATT

With the single exception of the reduction studies described by Watt and Fernelius,¹ the only available information relative to reactions of metal oxides in liquid ammonia consists of a number of incidental qualitative observations² together with certain partially erroneous³ results on reactions of the acidic oxides of chromium, molybdenum and tungsten published by Rosenheim and Jacobssohn.⁴ The experiments described in this paper represent the first of a series of studies initiated for the purpose of providing information on the behavior of metal oxides toward liquid ammonia and liquid ammonia solutions of ammonium salts (acids), alkali amides (bases) and strong reducing agents.

(1) Watt and Fernelius, *THIS JOURNAL*, **61**, 2502 (1939).

(2) For primary references see Fernelius and Watt, *Chem. Rev.*, **20**, 213 (1937).

(3) Davies and Watt, forthcoming publication.

(4) Rosenheim and Jacobssohn, *Z. anorg. allgem. Chem.*, **50**, 297 (1906).

Experimental

Methods.—Unless otherwise indicated, the experimental techniques were those employed by Watt and Fernelius.¹ All analytical data were obtained using standard methods of analysis.

Materials.—All materials were carefully dried before use. All chemicals other than the oxides were either reagent grade materials or consisted of commercial products which were subjected to careful purification.

Cobalt(III) Oxide.—Baker "reagent grade" oxide was dried for ten hours at 100° and used without further treatment.

Anal. Calcd. for Co_2O_3 : Co, 71.06. Found: Co, 70.75.

Cobalt(II) Oxide.—The most satisfactory method for the preparation of this material was found to be that of Le Blanc and Möbius.⁵ However, the use of this method in the original or in modified form, as well as other known methods,⁶ failed to yield a product of the desired composition.

(5) Le Blanc and Möbius, *Z. physik. Chem.*, **A142**, 151 (1929).

(6) For details see Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1937, Vol. XIV, pp. 558-563.