(42 g.) fractionally distilled *in vacuo* with the results given in Table II.

TABLE II

RESULTS OF ANALYSES OF FRACTIONS OBTAINED BY DISTILLING METHYL ESTERS OF SATURATED ACIDS OF EXPRESSED *Guanábana* SEED OIL

Fractions		1	2	3	4
Temperature, °C.		155–165	165–171	171–179	179–184
Pressure, mm.		3.5	3.5	3.5	4.0
Iodine no.		2.55	4.26	6.42	10.51
Sap. no. esters satd. acids		208.9	203.4	200.0	195.9
Esters unsat. acids, %		2.55	4.26	6.42	10.51
Esters satd. acids, %		97.45	95.74	93.58	89.49
Mean mol. wt. esters satd. acids		268.0	275.2	279.8	285.8
Composition of methyl esters satd. acids, %	Myristic	7.47	....	...	...
	Palmitic	84.76	75.05	58.81	38.05
	Stearic	...	15.80	30.10	47.00

There was practically no residue after the vacuum distillation. The iodine and saponification numbers of the different fractions were determined and the mean molecular weights of the esters calculated according to the Baughman and Jamieson[5] method. These results are recorded in Table II. To confirm the data in Table II the acids were isolated from the different fractions and fractionally crystallized from 95% ethyl alcohol.

Myristic Acid.—An acid melting at 54.6° was obtained from fraction 1. An anilide prepared from this same acid had a melting point of 84.0°; mix melting point, 83.5°. These two melting points, corresponding very closely to those of myristic acid and its anilide, were considered evidence of myristic acid.

Palmitic Acid.—Fractions 1, 2, 3 and 4 gave an acid melting at 62.9°. The anilide prepared

(5) Baughman and Jamieson, THIS JOURNAL, **42**, 157 (1920).

from this acid had a melting point of 90.0°; mix melting point, 89.8°, which two melting points corresponded very closely to those of palmitic acid and its anilide and were considered evidence of palmitic acid.

Stearic Acid.—Fractions 2, 3 and 4 yielded an acid melting at 69.1°. The anilide prepared from this acid had a melting point of 93°; mix melting point, 92.8°. As these two melting points corresponded very closely to those of stearic acid and its anilide, they were considered evidence of stearic acid.

TABLE III

UNSATURATED AND SATURATED ACIDS IN EXPRESSED *Guanábana* SEED OIL

Acids	In unsatd. acids, %	In satd. acids, %	In original oil, %	Glycerides in oil, %
Linoleic	16.63	...	11.64	12.11
Oleic	83.37	...	58.38	61.01
Myristic	...	1.45	0.32	0.34
Palmitic	...	73.55	16.20	16.99
Stearic	...	25.00	5.51	5.76

Summary

The characteristics and composition of hot expressed *guanábana* (*Annona muricata* L.) seed oil have been determined.

SAN JUAN, PUERTO RICO   RECEIVED OCTOBER 19, 1942

Ionization and Dissociation by Electron Impact: Butene-1

BY D. P. STEVENSON[1]

In this communication the results of a mass-spectrographic investigation of the ionization and dissociation of butene-1 by electron impact are reported. The instrument and general technique have been described in an earlier article.[2] The sample of butene-1 was a Phillips Petroleum Company product which was given to us by the Gulf Oil Company Research Laboratories.

(1) Westinghouse Research Fellow, 1940–1942. Present address: Shell Development Company, Emeryville, California.

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

TABLE I

APPEARANCE POTENTIALS OF VARIOUS IONS IN THE MASS SPECTRUM OF BUTENE-1

Ion (X⁻)	A(X⁺), e. v.	Process
$C_4H_8^+$	9.65 ± 0.1	$1\text{-}C_4H_8 \longrightarrow C_4H_8^+ + e^-$
$C_4H_7^+$	11.07 ± .1	$C_4H_7^+ + H + e^-$
$C_3H_5^+$	11.65 ± .1	$C_3H_5^+ + CH_3 + e^-$
$C_3H_4^+$	11.7 ± .2	$C_3H_4^+ + CH_4 + e^-$
$C_3H_3^+$	13.8 ± .2	$C_3H_3^+ + ? + e^-$
$C_2H_5^+$	11.97 ± .1	$C_2H_5^+ + C_2H_3 + e^-$
$C_2H_3^+$	13.6 ± .3	$C_2H_3^+ + C_2H_5 + e^-$
CH_3^+	<20	$CH_3^+ + ? + e^-$

In Table I the appearance potentials of some of the ions in the mass spectrum of butene-1 are summarized. These quantities were determined in the usual manner.[2] The initial break of the ionization efficiency curve of argon was used to correct the voltage scale for the "contact potential" of the oxide coated, platinum filament. The ionization potential of argon, $I^x(A) = 15.76$ e. v., was taken from the tables of Bacher and Goudsmit.[3]

The rather small difference between the appearance potentials of the parent ions in the mass spectra of propylene $(A(C_3H_6^+) = 9.7_6 \pm 0.1$ e. v.)[4] and butene-1 $(A(C_4H_8^+) = 9.6_5 \pm 0.1$ e. v.) is surprising in view of the 0.8 e. v. difference between the corresponding appearance potentials in propane[4] and the butanes.[2] The marked difference in the nature of the electron removed from a saturated and an unsaturated hydrocarbon is clearly shown by the equality of the appearance potentials of the parent ions in the spectra of n- and iso-butane and the 0.8 e. v. difference between the vertical ionization potentials of butene-1 (9.6_5) and isobutylene (8.8_7).[4] It will be noted that the spectroscopically determined ionization potential of *trans*-butene-2 (9.2 e. v.)[5] lies between the electron impact values for butene-1 and isobutylene.

Inasmuch as there are four possible structures for the ion, $C_4H_7^+$, formed from butene-1, it is not possible to discuss the appearance potential of this ion in detail. Butene-1 differs from the other olefinic molecules which have been studied in that the difference between the appearance potentials of the parent ion, $C_4H_8^+$, and the ion, $C_4H_7^+$, is but 1.4 e. v. instead of the 2.2 e. v. found for the corresponding differences in ethylene, propylene and isobutylene.[4] Since this difference is about 1.2 e. v. for ethane, propane and the butanes, one is led to suspect that in the reaction, $1\text{-}C_4H_8 \rightarrow C_4H_7^+ + H + e^-$, it is one of the methyl hydrogens, $i.$ $e.$, an essentially paraffinic hydrogen, that is lost. The relative abundance of the $C_4H_7^+$ ion in the spectrum of butene-1 is considerably greater than in the spectrum of isobutylene. It

is not clear how this observation is to be reconciled with the much greater relative abundance of the butyl ion in the spectrum of isobutane than in normal butane.

It seems reasonable to assume that no molecular arrangement accompanies the formation of the $C_3H_5^+$ ion from either butene-1 or isobutylene. Thus, butene-1 should give the allyl ion while isobutylene should give the isomeric $CH_3CCH_2^+$. Isobutylene is 0.156 e. v.[6] more stable than butene-1, hence the appearance potentials of C_3H_5 in the spectra of butene-1 (11.6_5) and isobutylene (11.5_1)[4] lead to the surprising suggestion that the allyl radical ion is 0.30 e. v. less stable than its unsymmetrical isomer, $CH_3CCH_2^+$. If the value of the appearance potential of the allyl ion in the butene-1 spectrum is combined with the appearance potential of the ion of the same formula in the propylene spectrum, $A(C_3H_5^+) = 11.9_6$ e. v., in the manner previously described,[7] one finds for the dissociation energy of the first hydrogen from methane, $D(CH_3\text{-}H) = 4.7_7 \pm 0.2$ e. v. This is greater, by more than the experimental error, than the value $D(CH_3\text{-}H) = 4.4_0 \pm 0.1$ e. v. suggested by considerable electron impact data on ethane,[7] propane,[7] the butanes,[7] n-propyl chloride[4] and methane and the methyl radical.[8] Kistiakowsky and his co-workers[9] found $D(CH_3\text{-}H)$ to be 4.43 $\pm$ 0.05 e. v. from kinetic data on the rate of bromination of methane, in perfect agreement with the electron impact value. The difference, $4.77 - 4.40 = 0.37$ e. v., can be assigned to the lower limit of the activation energy of the reaction $CH_2CHCH_2^+ + CH_3 \rightarrow CH_3CH_2CHCH_2^+$ provided that $CH_2CHCH_2^+ + H \rightarrow C_3H_6^+$ requires no activation energy. If such is the case, the allyl ion is at least 0.09 e. v. more stable than the isoallyl ion. It will be shown below that other electron impact data are most easily explained if an activation energy for the addition of radicals to the vinyl ion is assumed.

The appearance potential of $C_3H_4^+$ in the butene-1 spectrum is in good agreement with the value one may deduce from thermochemical data

(3) R. F. Bacher and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., New York, N. Y. The ionization potential has been corrected for the new value of the conversion factor for cm.$^{-1}$ to e. v. 1 e. v. = 8066 cm.$^{-1}$ The old value $I^x(A) = 15.69$ was used in ref. 2. *Cf.* ref. 8. The older data quoted in this paper have been corrected for this difference.

(4) D. P. Stevenson and J. A. Hipple, THIS JOURNAL, **64**, 2769 (1942).

(5) W. C. Price and W. T. Tutte, *Proc. Roy. Soc.* (London), **A174**, 207 (1940).

(6) F. D. Rossini, *Chem. Rev.*, **27**, 1 (1940).

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

(8) J. A. Hipple and D. P. Stevenson, *Phys. Rev.*, Feb. (1943). The ionization potentials of the methyl and ethyl radicals reported in this paper are 10.0_0 and 8.6_0 e. v., respectively. The old value of $I^x(A)$, 15.69 e. v., was used to correct the voltage scale. These values should be raised to 10.07 and 8.67 e. v. for comparison with the appearance potentials given in Table I of this paper.

(9a) H. C. Anderson, G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942).

(9b) E. R. Van Artsdalen, *ibid.*, **10**, 653 (1942).

and the observed vertical ionization potential of allene.[10] Since the ionization potential of methyl acetylene is 11.25 e. v.,[11] over a volt higher than that of allene, the $C_3H_4{}^+$ has the allene rather than the CH_3CCH structure. The value of $A(C_3H_3{}^+)$ = 13.8 ± 0.2 e. v. indicates that the accompanying unionized products are either $CH_4 + H$ or $CH_3 + H_2$, and that no large activation energy is necessary for the reverse reaction.

Direct measurement[8] has confirmed the value 8.67 e. v.[2] for the ionization potential of the ethyl radical. Thus the appearance potential of $C_2H_5{}^+$ in the butene-1 spectrum, 11.97 ± 0.1 e. v. leads to $D(C_2H_5—C_2H_3) = 3.3_0 ± 0.2$ e. v. If the reaction $C_2H_5{}^+ + C_2H_3 \rightarrow 1\text{-}C_4H_8{}^+$ requires an activation energy, this value of D is an upper limit. The value 3.43 e. v. for $D(C_2H_5—C_2H_5)$ is well established.[7,9] The relative values of these dissociation energies appear at first sight to contradict chemical evidence which shows olefinic compounds to be more stable with respect to pyrolysis than the related saturated hydrocarbons. If, as is conceivable, the reaction $C_2H_5 + C_2H_3 \rightarrow 1\text{-}C_4H_8$ requires an activation energy of more than 0.5 e. v. while the reaction $C_2H_5{}^+ + C_2H_3 \rightarrow 1\text{-}C_4H_8{}^+$ has none, the chemical evidence and electron impact results are reconciled.

The appearance potential of $C_2H_3{}^+$ in the ethane spectrum (15.2 e. v.[2]) combined with the heat of hydrogenation of ethylene (1.42 e. v.[6]) leads to an estimated 13.8 e. v. for the heat of the reaction, $C_2H_4 \rightarrow C_2H_3{}^+ + H + e^-$. Since $\Delta H_{298.1}^0 =$ 1.073 e. v. for the reaction $1\text{-}C_4H_8 = 2C_2H_4$, and C_2H_5 is 1.7 e. v. more stable than $C_2H_4 + H$, one finds $A_{calc.}(C_2H_3{}^+)$ for $1\text{-}C_4H_8 \rightarrow C_2H_3{}^+ + C_2H_5 + e^-$ equal to 13.2 e. v. The observed value of 13.6 e. v. suggests an 0.4 e. v. activation energy for the reaction $C_2H_3{}^+ + C_2H_5 \rightarrow 1\text{-}C_4H_8{}^+$. Kusch, Hustrulid and Tate[12] found 14.2 e. v. for the appearance potential of the vinyl ion in the spectrum of ethylene, a value to be compared with the 13.8 e. v. calculated above. This comparison leads to an 0.4 e. v. activation energy for the addition of an hydrogen atom to a vinyl ion.

Taking the value of $D(C_2H_5—C_2H_3)$ found above (3.3_0), 0.4 e. v. for the activation energy of addition of an ethyl radical to a vinyl ion and the appearance potential of the vinyl ion in the spec-

trum of 1-butene (13.6 e. v.), one obtains 9.9 e. v. for the ionization potential of the vinyl radical.

In Table II we present a summary of the heats of dissociation obtained from electron impact data and those which may be derived from them by direct combination with thermochemical data. The necessary heats of formation were taken from either Rossini's review article[6] or the compilation of Bichowsky and Rossini.[13]

TABLE II

HEATS OF DISSOCIATION, $D(R'—R'')$, IN E. V., FOR THE REACTIONS $R'—R'' = R' + R'' - D$

R''	R' = H	CH₃	C₂H₅	C₂H₃	Cl
H	4.502	...	..	..	...
CH₃	4.40	3.62	..	..	...
C₂H₅	4.2₀	3.52	3.43	..	...
C₂H₃	3.95	3.43	3.3₀	3.32	...
Cl	4.4₆	3.5₀	3.45	3.1	2.50
$I^*(R')$	13.5	10.07	8.67	9.9	12.9

We have made no corrections for the thermal excitation of the molecules and radicals above their zero point energies. Since the corrections probably cancel to a large extent for the radicals, the heats of dissociation can be taken as referring to 298°K., the reference temperature for the heats of formation of the molecules.

The C_4 region of the mass spectrum of butene-1 (given in Table III) has qualitatively the same pattern as that of isobutylene. The relative current of $C_4H_7{}^+$ for 50 volt electrons is about 10% greater in butene-1 than in isobutylene. The ratios of the currents of $C_4H_6{}^+:C_4H_5{}^+$ and $C_4H_4{}^+:C_4H_3{}^+$ are roughly the same in the spectra of both butenes.

The ion $C_3H_6{}^+$ is twice as abundant in the spectrum of isobutylene as in that of butene-1 while $C_3H_5{}^+$ and $CH_3{}^+$ are 20 and 30% more abundant in the spectrum of butene-1. These relative abundances are consistent with the usually assumed greater reactivity of the bonds to a carbon atom adjacent (α-carbon atom) to an unsaturated carbon atom.

As might be expected from a comparison of the structures involved, $C_2H_5{}^+$ and $C_2H_3{}^+$ are much more abundant (almost by a factor of 2) in the spectrum of butene-1. In this respect the spectra of the butenes differ more from one another than do the spectra of the two butanes.

With respect to their tendency to give ionic fragments, the butenes are more alike than are the butanes. This is clearly brought out by a comparison of the fraction of the ion currents carried by the parent ions. These fractions are $n\text{-}C_4H_{10}$

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

(11) T. M. Sugden, A. D. Walsh and W. C. Price, *Nature*, **148**, 375 (1941).

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

(13) F. R. Bichowsky and F. D. Rossini, "Thermochemistry," Reinhold Publishing Co., New York, N. Y., 1936.

TABLE III

MASS SPECTRUM OF BUTENE-1

m/e V-	56 $C_4H_8{}^+$	55 $C_4H_7{}^+$	54 $C_4H_6{}^+$	53 $C_4H_5{}^+$	52 $C_4H_4{}^+$	51 $C_4H_3{}^+$	50 $C_4H_2{}^+$	49 $C_4H{}^+$	48 $C_4{}^+$
20	100	30.5	2.6	2.1	. . .	. .	. .	. . .	. . .
30	117	53.0	6.0	11.4	1.5	2.5	0.7	. . .	. . .
40	122	59.0	7.0	14.9	3.3	8.4	5.7	. . .	. . .
50	127	61.1	7.2	15.4	3.6	10.5	10.1	2.0	0.2
60	130	64.0	7.3	15.8	3.6	11.0	11.4	. . .	. . .

m/e V-	42 $C_3H_6{}^+$	41 $C_3H_5{}^+$	40 $C_3H_4{}^+$	39 $C_3H_3{}^+$	29 $C_2H_5{}^+$	18 $C_2H_4{}^+$	27 $C_2H_3{}^+$	26 $C_2H_2{}^+$	15 $CH_3{}^+$	14 $CH_2{}^+$
20	3.9	153	8.2	12.0	. .	. .	. .	. .	. .	. . .
30	5.2	275	17.7	66.0	34	71	41	4.5	3.2	. . .
40	5.2	320	21.0	91.1	47	95	85	16.5	7.6	. . .
50	5.2	335	22.1	98.0	48	97	95	24.5	9.6	2.9
60	. . .	. . .	22.8	99.1	49	98	99	28.0	10.4	3.7

The relative abundances have been corrected for the presence of C^{13} in its natural abundance of 1.1%. The dots indicate no measurement was made.

8.0%, i-C_4H_{10} 4.3%, l-C_4H_8 12.7% and i-C_4H_8 14.7%. This comparison is specifically for 50 volt electrons, but it holds approximately for bombardment by electrons of from 30 to 100 volts energy. It will be noted that the unsaturates have considerably less tendency to dissociate after ionization by electron impact than do the saturates.

Summary

The appearance potentials and relative abundances of a large portion of the ions in the mass spectrum of butene-1 are reported. The vertical ionization potential of butene-1 is found to be $9.6_5 \pm 0.1$ e. v., 0.8 e. v. higher than that of isobutylene. The heat of dissociation of the C_2H_5—C_2H_3 bond is $3.3_0 \pm 0.2$ e. v. and the ionization potential of the vinyl radical is $9.8_7 \pm 0.2$ e. v. The mass spectrum of butene-1 is briefly compared with those of isobutylene and the butanes. A summary of the heats of dissociation deduced from electron impact data is included.

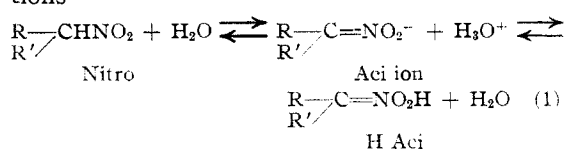## The Ionization Constants of Aci and Nitro Forms of Some Nitroparaffins

BY DAVID TURNBULL AND SAMUEL H. MARON

It is well known that nitroparaffins possessing a hydrogen atom on the α-carbon exist in two tautomeric forms, nitro and aci, both of which exhibit acidic properties. The anions produced in the ionization of the two forms are apparently indistinguishable. The ionization equilibria involved can be represented in general by the equations

$$\underset{\text{Nitro}}{\overset{R}{\underset{R'}{>}}CHNO_2} + H_2O \rightleftarrows \underset{\text{Aci ion}}{\overset{R}{\underset{R'}{>}}C{=}NO_2{}^-} + H_3O^+ \rightleftarrows$$

$$\underset{\text{H Aci}}{\overset{R}{\underset{R'}{>}}C{=}NO_2H} + H_2O \quad (1)$$

where R and R' may be either hydrogen atoms or alkyl groups. According to the evidence deduced from kinetic studies,[1] the equilibrium between the

(1) Maron and LaMer, Ann. New York Acad. Sciences, Vol. XXXIX, 355 (1940).

nitro and aci forms appears to be established through the aci ion rather than by direct migration of a proton from the α-carbon to the oxygen.

The *concentration* ionization constant of the nitro form, K_N, may be defined by the equation

$$K_N = [\text{Aci}^-][H_3O^+]/[\text{Nitro}] \quad (2)$$

where the brackets are taken to denote concentrations in moles per liter. In turn, the ionization constant of the aci form, K_{aci}, is given by the equation

$$K_{aci} = [\text{Aci}^-][H_3O^+]/[\text{H Aci}] \quad (3)$$

On division of (3) by (2) the tautomeric equilibrium constant, K_T, between the two forms follows as

$$K_T = [\text{H Aci}]/[\text{Nitro}] = K_N/K_{aci} \quad (4)$$

Junell[2] determined the "apparent" ionization

(2) Junell, Dissertation, Upsala, Sweden, 1935.