narily does not dissociate in liquid phase. It is to be noted that the only saturated hydrocarbons resulting from reactions 2 or 3 are branched and, in some cases, cyclic. This is in accord with the results: the ozone-resistant dimer contained no *n*-dodecane.

The yield of hydrogen, which is not balanced by the extent of unsaturation in the dimers, trimers and tetramers necessitates the assumption that the higher polymers must contain rings or more than one double bond per molecule. A reaction scheme involving scission of a carbon-hydrogen bond in an olefin yielding a hydrogen atom and a radical would be incompatible with the experimental findings. However, the production of hydrogen in the radiolysis of paraffins has been attributed largely to a molecular process.[6,23,24] Molecular production of hydrogen from an olefin molecule would result in the formation of a diene which would be very reactive in chain polymerization.

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Ionization Potentials of Some Olefins, Di-olefins and Branched Paraffins

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The ionization potentials of a number of olefins, cycloölefins, di-olefins and branched paraffins have been measured by electron impact. The results obtained have been compared where possible with ionization potentials obtained by photoionization and by ultraviolet spectroscopy, as well as with earlier electron impact data. Values presented for a number of compounds which had not been investigated previously are consistent with structural considerations. Some inconsistencies in the earlier electron impact data are discussed.

Introduction

The ionization potentials of a large number of hydrocarbon molecules have been measured by electron impact, and a recent survey[2] shows that for most of these compounds the published data are in satisfactory agreement. For a number of compounds, on the other hand, the existing data show a remarkable spread. For instance, in the values for isobutane and isobutene a spread of nearly 1.0 v. is found among values obtained by different workers. In other cases, as for the pentanes and hexanes, the published ionization potentials do not reflect the structural differences in the manner to be expected. For other branched olefins and for di-olefins very few values are available. The present work represents an attempt to resolve some of the discrepancies and to provide electron impact values for a number of compounds which have not been investigated previously.

Experimental

The method of obtaining the ionization efficiency curves for the compound and for the added standard gas, usually krypton or xenon, has been described previously.[3]

Materials.—The authors are greatly indebted to Professor K. B. Wiberg and Mr. Jerry Albin of the University of Washington for the gift of a sample of cyclopropene. The other compounds were NBS standard samples or commercial chemicals of high purity.

Results and Discussion

(a) **Branched Paraffins.**—The values obtained for five branched paraffins are given in Table I, together with the earlier values obtained by electron impact.[4–8] Also included in the table are ionization potentials measured by photoionization[9] and two sets of values calculated using slightly different parameters.[10] It is of interest to note that the values obtained in this work parallel almost exactly the photoionization data, the former being in each case higher by 0.24–0.30 v. Since the transitions brought about by electron impact and by photon impact should both be vertical transitions, this constant difference must arise from a difference in the means of interpreting the ionization threshold in the two methods. By comparison with the earlier electron impact data for isobutane, the present data are in best agree-

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TABLE I

IONIZATION POTENTIALS OF BRANCHED PARAFFINS

Compound	Electron impact		Photo-ionization[9]	Calcd.[10]
	Lit.	This work		
Isobutane	10.3 ± 0.2[4] 11.06[5] 10.7 ± 0.2[6] 10.34 ± 0.1[7] 9.8 ± 0.2[8]	10.79	10.55	10.82, 10.63
2-Methylbutane	10.1 ± 0.2[1]	10.60	10.30	10.67, 10.43
2-Methylpentane	10.0 ± 0.2[4]	10.34	10.09	....
3-Methylpentane	9.8 ± 0.2[4]	10.30	10.06	....
2,3-Dimethylbutane	10.1 ± 0.3[4]	10.24	10.00	10.48, 10.21

ment with the value of Fox and Langer.[6] The values of Mitchell and Coleman[5] and of Baker and Tate[8] appear to lie outside the expected range. For 2-methylpentane and 3-methylpentane the ionization potentials are found to be nearly the same, and appreciably lower than for 2-methylbutane, as would be expected from structural considerations. The photoionization data show a similar relation. The ionization potential of 2,3-dimethylbutane is lower than that of the other branched hexanes, rather than higher as indicated by Mitchell and Coleman's data. This is in agreement with the difference shown by the photoionization results and is again the relation which would be predicted.

In view of the difference between the electron impact and the photoionization data, a choice between the two sets of calculated values cannot be made, but it may be noted that the magnitude of the decrease in ionization potential with increasing substitution is reproduced very closely in both sets.

(b) **Olefins.**—The ionization potentials found for a number of straight and branched olefins are given in Table II. For comparison, the electron impact values published earlier,[5,6,11–14] values obtained by photoionization,[9,15] and by ultraviolet spectroscopy,[16] and values calculated by molecular orbital methods[10,17] also are shown. A comparison of the present measurements with the photoionization data shows, as before, a close parallelism. For the olefins the difference between values obtained by the two methods, 0.1–0.2 v., is smaller than for the paraffins. The agreement among the electron impact data for 1-butene is satisfactory. For isobutene, the value found in this work is in good agreement with that found by Honig[13] and with the photoionization result.[9] This supports the prediction from structural considerations that the ionization potential of isobutene would be very close to those of *cis*- and *trans*-2-butene. The evidence therefore favors a vertical ionization potential of 9.2–9.3 v. for isobutene, and the lower values of about 8.8 v.[6,14] appear to lie outside the expected range.

TABLE II

IONIZATION POTENTIALS OF OLEFINS

Compound	Electron impact		Photo-ionization	Spectroscopy	Calcd.
	Lit.	This work			
1-Butene	9.65[11] 9.65[12] 9.76[13] 9.77[6] 10.0[5]	9.76	9.58[15]	..	9.70[10]
Isobutene	8.78[6] 8.86[14] 9.35[13] 9.65[5]	9.26	9.23[9]	..	9.28[10]
cis-2-Butene	9.24[6] 9.30[13] 9.41[12]	9.34	9.13[9]	..	9.28[10] 9.27[17]
trans-2-Butene	9.13[12] 9.28[13]	9.27	9.13[9]	9.2[16]	9.28[10] 9.29[17]
1-Pentene	9.66[13]	9.67	9.50[9]	..	9.67[10]
3-Methyl-1-butene	....	9.60	9.51[9]	..	...
2-Methyl-1-butene	....	9.20	9.12[9]	..	...
cis-2-Pentene	....	9.11	...	..	...
trans-2-Pentene	....	9.06	...	..	...
3-Methyl-2-butene	8.85[13]	8.89	8.68[9]	8.8[16]	8.81[10] 8.88[17]
Tetramethylethylene	....	8.53	...	8.4[16]	8.40[10] 8.52[17]

For *cis*- and *trans*-2-butene the electron impact, photoionization and calculated values are in quite close agreement. The electron impact values suggest that I (*trans*) is slightly less than I (*cis*), but this is not confirmed by the photoionization data. The value of 9.2 v. for I (2-butene) obtained from ultraviolet spectroscopy by Price and Tutte[16] some years ago is in excellent agreement with the other data, as are the values for 3-methyl-2-butene and tetramethylethylene. One particularly striking feature of the olefin data is the success of the calculations of Hall[17] and of Franklin[10] in reproducing the measured ionization potentials to within 0.1 v.

An interesting consequence of structural effects can be seen by comparing I (2-butene) with I (1-butene), the former being about 0.5 v. less. Similarly I (2-pentene) is about 0.6 v. less than (1-pentene). A comparable decrease (0.5 v.) occurs on going from 1-butene to isobutene and from 1-pentene to 2-methyl-1-butene (0.47 v.). These changes are consistent with an increase in hyperconjugational effects as methyl groups are added around the double bond.

(c) **Cycloölefins.**—The ionization potential data for cycloölefins are summarized in Table III. The ionization potential of the interesting compound cyclopropene has not been measured previously. The observed value, 9.95 v., is nearly the same as the ionization potential of propylene, 9.84

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v.[13] It may be noted that the ionization potential of cyclopentene found in this work, 9.27 v., is similarly close to the ionization potential of 2-pentene, 9.11 v., and that of cyclohexene, 9.18 v., is close to that of 2-hexene, 9.16 v.[13] and 3-hexene, 9.12 v.[13] The agreement of the value reported here for cyclopentene with the photoionization value, 9.01 v.,[9] suggests that the earlier electron impact result of Hissel[18] is considerably too high. For cyclohexene the agreement with the electron impact value of Morrison and Nicholson,[19] the photoionization value,[15] the spectroscopic value[16] and the calculated value[10] is quite satisfactory.

TABLE III

IONIZATION POTENTIALS OF CYCLOÖLEFINS

Compound	Electron impact Lit.	Electron impact This work	Photoionization	Spectroscopy	Calcd.
Cyclopropene	....	9.95	....	..	...
Cyclopentene	10.2[18]	9.27	9.01[9]	..	...
Cyclohexene	9.7[18] 9.24[19]	9.18	8.945[15]	9.2[16]	9.16[10]

(d) Di-olefins.—The ionization potentials found for four pentadienes and for 1,5-hexadiene are given in Table IV. For comparison, values for allene and the butadienes measured previously[20] and the available values from the literature[6,15,21–25] have been included. As would be expected, the only conjugated pentadiene has an ionization potential much lower (0.5 v.) than the three non-conjugated ones. The differences among the latter are small and probably result from hyperconjugational effects.

TABLE IV

IONIZATION POTENTIALS OF DI-OLEFINS

Compound	Electron impact Lit.	Electron impact This work	Photoionization	Spectroscopy	Calcd.
Allene	10.16[20] 10.0[21]	..	...	10.19[22]	....
1,2-Butadiene	9.57[20]	..	...	....	....
1,3-Butadiene	9.18[20] 9.2[6] 9.24[19]	..	9.07[15]	*cis* 8.75[23] *trans* 9.07[24]	 *trans* 8.81[25]
1,2-Pentadiene	....	9.42	...	....	....
2,3-Pentadiene	....	9.26	...	....	....
1,3-Pentadiene	....	8.68	...	....	....
1,4-Pentadiene	....	9.58	...	....	9.28[10]
1,5-Hexadiene	....	9.51	...	....	....

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