from CCl_4 to diethyl ether to triethylamine. Roughly tenfold enhancements in intensity were observed between the free hydroxyls in CCl_4 and the solvent bonded groups in triethylamine. Tsubomura[19] measured the intensity of the free hydroxyl absorption in CCl_4 and *n*-heptane. These intensities were compared to values obtained when acceptor molecules, *viz.*, chlorobenzene, acetonitrile, ethyl acetate, were added to the solutions. Intensities were increased by as much as fivefold by means of the stronger acceptors.

It is apparent that hydrogen bonding causes profound changes in the nature of the hydroxyl vibration. Francis[15] has shown that these results are not explainable on the basis of a simple electrostatic picture for this bond.[20] Both Tsubomura and Barrow show that this marked enhancement in hydroxyl intensity upon hydrogen bonding can be accounted for by attributing to the bond a variable ionic character.

The two slopes in Fig. 3 give values for the integrated intensity of the carbon–hydrogen stretching bands of acids in the neighborhood of 3000 cm.$^{-1}$. These values are 0.44 for the saturated acids and 0.49 for the conjugated acids. The difference between these values should not be regarded as significant. It is possible, however, that the carbon–hydrogen bonds on aromatic or dienoic systems give rise to absorptions of slightly greater intensity than aliphatic bonds. Francis[21] reported a value of 0.78 intensity unit for the intensity of the carbon–hydrogen bonds of methylene groups in aliphatic hydrocarbons. Half this value (0.39) agrees approximately with the value of 0.44 intensity unit obtained for aliphatic carbon–hydrogen absorption in the present work. The slightly higher value of the present result may be explained by the fact that the integration involved here included the entire wing of the carbon–hydrogen band, while Francis terminated his integrations at arbitrary limits.

Intensities of free and bonded carbonyl stretching absorptions, as determined using eq. 2, are shown in Table III. Concentrations for use in this equation were calculated from the dissociation constants obtained from studies of the free hydroxyl band. These intensities are seen to be characteristic for each type of absorption. Because of the complicating effects of the 6μ water band the values in Table III are only good to within about 10%.

TABLE III

INTENSITIES OF FREE (A_{mon}) AND BONDED (A_d) CARBONYL GROUPS OF ACIDS IN CARBONYL STRETCHING REGION

Acid	A_{mon}, intensity units	A_d, intensity units
Acetic	3.9	4.5
Propionic	3.3	4.5
Benzoic	4.9	6.0
o-Toluic	4.4	5.8

As in the case of the hydroxyl bands, it is found that there is an increase in intensity upon conjugation. This observation is in agreement with the work of previous investigators.[17] An enhancement in carbonyl intensity upon hydrogen bonding is also evident. This enhancement is not so pronounced as is the similar effect involving the hydroxyl group.

SILVER SPRING, MD.

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[20] N. D. Coggeshall, *J. Chem. Phys.*, **18**, 978 (1950).

[21] S. A. Francis, *ibid.*, **18**, 861 (1950).

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Ionization and Dissociation of Allene, Propyne, 1-Butyne, and 1,2- and 1,3-Butadienes by Electron Impact; the $C_3H_3^+$ Ion

BY J. COLLIN[1] AND F. P. LOSSING

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The ionization potentials of allene, 1,2-butadiene and 1,3-butadiene have been found to be 10.16, 9.57 and 9.18 volt, respectively. The appearance potentials of the $C_3H_3^+$ ion from these compounds and from propyne and 1-butyne have been measured. From the results it is concluded that the $C_3H_3^+$ ion formed from these compounds by electron impact has the propargyl ($CH\equiv C-{}^+CH_2$) structure in each case, and that the hydrogen migration required to form this ion from 1.3-butadiene must occur with almost zero activation energy. The following bond dissociation energies have been derived: $D(C_3H_3\text{-}H)$ in allene $\leqslant 81.2$ kcal./mole, $D(C_3H_3\text{-}H)$ in propyne $\leqslant 82.8$ kcal./mole, $D(C_3H_3\text{-}CH_3)$ in 1,2-butadiene $\leqslant 68.2$ kcal./mole, $D(C_3H_3\text{-}CH_3)$ in 1-butyne $\leqslant 67.5$ kcal./mole. The heat of formation of C_3H_3 radical = 75 kcal./mole, and of $C_3H_3^+$ ion = 265 kcal./mole.

Introduction

The electron impact technique for the determination of appearance potentials of gaseous ions has been used extensively and undoubtedly has thrown considerable light on ionization potentials of molecules and free radicals. In a number of cases, it has been possible to deduce quite satisfactory values for certain bond dissociation energies. In combination with known heats of formation of molecules, appearance potential data have been widely used to calculate heats of formation of radicals and molecular and radical ions. In some cases a choice between different possible structures of ions and radicals can be made, and a mechanism for their formation can be suggested.

In connection with a mass spectrometric study of the mercury photosensitized decomposition of allene and butadienes, we have determined the appearance potentials of certain ions in the mass spectrum of these molecules. Of particular interest is the C_3H_3 ion and radical since, on the one hand, the radical plays an important role in the

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[1] National Research Council of Canada Postdoctorate Fellow 1956–1957.

sensitized decompositions and, on the other hand, the structure of this ion has been the subject of conflicting interpretations.[2]

Experimental

The appearance potentials were determined by means of a Nier type mass spectrometer, using krypton as a calibrating gas. When making such measurements it is always a problem to decide which method should be used to interpret the experimental data. Therefore special attention has been given to this point and a rather extensive study of the ionization and appearance potentials of hydrocarbons and other compounds has been made, in which the results obtained by the vanishing current method, the linear extrapolation method, and a semi-log method have been compared. The detailed results will be published elsewhere, but the following conclusions have been drawn from the experimental evidence. The linear extrapolation definitely can be excluded, since in many cases the choice of the linear part of the ionization efficiency curve is quite subjective. It is quite often impossible to find any linear portion at all, especially for fragment ions. Both the vanishing current and the semi-log method yield satisfactory results for ionization potentials. In the case of fragment ions, however, the curves are often less steep than those of the standard gas, and the choice of the vanishing point is quite subjective. On the average, for both molecular and fragment ions, we found that the maximum deviation from the mean is often of the order of 0.1 v. or more in the vanishing current method, while in the semi-log method the deviations rarely exceed 0.05 v. The appearance and ionization potentials reported here are therefore those obtained by the semi-log method.[3] In certain cases where the ionization efficiency curves show a considerable tail, the results were evaluated by extrapolation of the voltage difference between the curves to zero ion current as proposed by Warren.[4] The errors given here represent the maximum deviation from the mean value of three measurements. Although this limit represents the reproducibility of the measurement, it can by no means be assumed that this is the absolute error of the measurement.

Materials.—The allene was prepared by Dr. L. C. Leitch of these laboratories. The propyne and butyne were obtained from Farchan Research Laboratories. The 1,3-butadiene was a Philips' Research Grade sample, and the 1,2-butadiene was a NBS standard sample.

Results and Discussion

(1) **Ionization Potentials.**—In Table I are given the experimental results as well as the available literature data obtained either by electron impact or by ultraviolet spectroscopy.

TABLE I

IONIZATION POTENTIALS OF ALLENE AND BUTADIENES

Substance	Ionization potential, v. This work		
	This work	Lit.[a]	Ultraviolet spectroscopy
Allene	10.16 ± 0.02	10.0[5]	10.19[6]
1,2-Butadiene	9.57 ± .02	...	...
1,3-Butadiene	9.18 ± .02	9.24[b]	8.75 *cis*[c] 9.07 *trans*[d]

[a] Electron impact data. [b] J. A. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, 20, 1021 (1952). [c] T. M. Sugden and A. D. Walsh, *Trans. Faraday Soc.*, 41, 76 (1945). [d] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **174A**, 220 (1940).

The ionization potential of allene has been measured previously by electron impact by Delfosse and Bleakney[5] who found 10.0 ± 0.2 v. Our value is 10.16 ± 0.02 v. These are in good agreement with the spectroscopic value of 10.19 v.[6] It is interesting to compare the ionization potential of allene with that of related molecules measured in the same instrument: propane 11.29 v., propylene 9.94 v. and propyne 10.32 v.[7] The value for allene lies between those for propylene and propyne. These values show, as do those for ethane (11.82 v.), ethylene (10.80 v.) and acetylene (11.41 v.),[7] that the olefinic molecule has a lower ionization potential than the corresponding paraffinic or acetylenic molecule. On this basis allene, being a diolefin with two adjacent double bonds, might be expected to have an even lower ionization potential. That this is not the case may be explained in the following way.

Allene has a structure somewhat analogous to the CO_2 molecule. In terms of localized orbitals this linear molecule is explained by referring to a digonal hybridized carbon atom like that in acetylenic compounds[8]: the hybrid orbitals formed out of the 2s and $2p_x$ orbitals of the carbon atom are paired with the oxygen $2p_x$ orbitals to form σ-bonds. The remaining oxygen 2s and 2p orbitals may be combined with carbon 2p orbitals to form π-bonds between these atoms. In the same way, the central carbon atom of allene is considered as being digonal, having thus more or less the same properties as the acetylenic carbon, whereas the outer carbon atoms are trigonally hybridized, like those in ethylene. As a result, the π-electrons of such a system would be expected to have an energy between that of propylene and that of propyne. One might say that the allene C–C bond has a certain triple bond character. Therefore, it may be expected that the ionization potential should be situated somewhere between the corresponding pure olefinic and pure acetylenic compounds, as is found experimentally.

Another interesting feature appears when comparing allene and 1,2- and 1,3-butadienes, for which the ionization potentials are 10.16, 9.57 and 9.18 v., respectively. The decrease in ionization potential when going from allene to 1,2-butadiene, *i.e.*, methylallene, is 0.59 v. The same effect is observed for ethylene and propylene, *i.e.*, methylethylene, for which the values are 10.80 and 9.94 v., respectively.[7] This may be explained by hyperconjugation and inductive effects. The methyl group attached to the allenyl radical may be hyperconjugated to the double bond of allene, resulting in a greater delocalization of π-electrons with, as a consequence, a lower ionization potential. Moreover, it is generally considered[8] that the trigonal carbon of a double bond is more electronegative than the tetrahedral carbon of the methyl group. This has the effect of giving a small polar character to the σ-bond between those atoms, the electronic charge tending to flow toward the trigonal carbon atom. This additional charge repels the π-electrons of the double bond and reduces further their ionization potential. These phenomena certainly play an important role in the observed effect.

In the case of 1,3-butadiene, one deals with a conjugated diene. It is well known that such an

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(2) (a) F. H. Field, *J. Chem. Phys.*, **20**, 1734 (1952); (b) F. H. Coats and R. C. Anderson, THIS JOURNAL, **79**, 1340 (1957).

(3) F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

(4) J. W. Warren, *Nature*, **165**, 810 (1950).

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

(6) L. H. Sutcliffe and A. D. Walsh, *J. Chem. Soc.*, 899 (1952).

(7) J. Collin and F. P. Lossing, to be published.

(8) C. A. Coulson, "Valence," Oxford University Press, 1953.

arrangement of double bonds causes a very important delocalization of the π-electronic charge, as a consequence of the different resonant species which must be considered as contributing to the true structure of this molecule, in order to account for the known chemical and physical properties of conjugated systems. This lowers considerably the levels of the possible excited states of the molecule, giving a further lowering of the ionization potential, found experimentally to be 0.39 v.

(2) **Appearance Potentials and the Nature of the $C_3H_3^+$ Ion.**—The appearance potentials of the $C_3H_3^+$ ion from allene, propyne, 1,2-butadiene, 1-butyne and 1,3-butadiene are given in Table II with the corresponding values from the literature. The value of $A(C_3H_3^+)$ from allene is significantly lower than that found by Delfosse and Bleakney. For propyne and 1-butyne the appearance potentials are only slightly greater than those of Coats and Anderson.[2b] The value of $A(C_3H_3^+)$ from 1,3-butadiene agrees with that of Fox and Langer[9] within the cited limits of error. Assuming the following modes of dissociation, the heat of formation of $C_3H_3^+$ ion (at 25°) can be calculated from these results.

Table II

Appearance Potentials of $C_3H_3^+$ and Other Ions

Substance	Ion	Appearance potential, v. This work	Lit.
Allene	$C_3H_3^+$	12.02 ± 0.03	12.5 ± 0.2[5]
Propyne	$C_3H_3^+$	12.00 ± .05	11.8 ± .1[2b]
1,2-Butadiene	$C_3H_3^+$	11.00 ± .03	....
	CH_3^+	14.4 ± .2	....
1-Butyne	$C_3H_3^+$	11.02 ± .05	10.8 ± .2[2b]
1,3-Butadiene	$C_3H_3^+$	11.71 ± .02	11.9 ± .2[9]
	$C_2H_3^+$	15.72 ± .08	....

$$CH_2{=}C{=}CH_2 + e \longrightarrow C_3H_3^+ + H + 2e \qquad (1)$$

$A(C_3H_3^+) = 12.02$ v. gives $\Delta H_f(C_3H_3^+) = 271$ kcal./mole

$$CH_3{-}C{\equiv}CH + e \longrightarrow C_3H_3^+ + H + 2e \qquad (2)$$

$A(C_3H_3^+) = 12.00$ v. gives $\Delta H_f(C_3H_3^+) = 269$ kcal./mole

$$CH_2{=}C{=}CH{-}CH_3 + e \longrightarrow C_3H_3^+ + CH_3 + 2e \qquad (3)$$

$A(C_3H_3^+) = 11.00$ v. gives $\Delta H_f(C_3H_3^+) = 260$ kcal./mole

$$CH_3{-}CH_2{-}C{\equiv}CH + e \longrightarrow C_3H_3^+ + CH_3 + 2e \qquad (4)$$

$A(C_3H_3^+) = 11.02$ v. gives $\Delta H_f(C_3H_3^+) = 263$ kcal./mole

$$CH_2{=}CH{-}CH{=}CH_2 + e \longrightarrow C_3H_3^+ + CH_3 + 2e \qquad (5)$$

$A(C_3H_3^+) = 11.71$ v. gives $\Delta H_f(C_3H_3^+) = 264$ kcal./mole

The following data were used: $\Delta H_f(CH_3) = 32.0$ kcal./mole, $\Delta H_f(H) = 52.1$ kcal./mole,[10] ΔH_f(allene) = 45.92 kcal./mole, ΔH_f(propyne) = 44.32 kcal./mole, ΔH_f(1,2-butadiene) = 38.77 kcal./mole, ΔH_f(1-butyne) = 39.48 kcal./mole and ΔH_f(1,3-butadiene) = 26.33 kcal./mole.[11] It is remarkable that the value of $\Delta H_f(C_3H_3^+)$ from 1,3-butadiene is the same, within the experimental error, as that from 1,2-butadiene, although the formation of this ion from 1,3-butadiene by process 5 requires the migration of a hydrogen atom in order that a CH_3 group be lost. If the neutral products were in fact a CH_2 group and an H atom formed separately as in the reaction

$$CH_2{=}CH{-}CH{=}CH_2 + e \longrightarrow C_3H_3^+ + H + CH_2 + 2e \qquad (6)$$

the heat of formation obtained for the $C_3H_3^+$ ion would be at least 80 kcal./mole lower than 264. It is difficult to imagine what structure such a $C_3H_3^+$ ion could have. On the other hand the good agreement between $\Delta H_f(C_3H_3^+)$ from 1,3-butadiene, using eq. 5, and the other values of $\Delta H_f(C_3H_3^+)$ requires that the necessary shift of a H atom in the ion proceed with almost zero activation energy. As discussed in a later section, a somewhat similar shift is required to explain the appearance potential of $C_3H_3^+$ from 2-butyne. It is interesting to note that in the mass spectrum of 1,3-butadiene there is a large metastable peak at mass 28.2, corresponding to the dissociation of $C_4H_6^+$ ion into $C_3H_3^+$ ion and neutral CH_3, for which a similar rearrangement is required.

The agreement for $\Delta H_f(C_3H_3^+)$ from allene, propyne, 1,2-butadiene, 1,3-butadiene and 1-butyne (Table III) suggests that the same ion is formed in each case. It is of interest to consider what the structure of this ion might be, and whether the $C_3H_3^+$ ion always has the same structure when produced from different molecules. In a study of the ionization and dissociation of cyclopropane, Field[2a] pointed out that values of $\Delta H_f(C_3H_3^+)$ calculated from appearance potentials of $C_3H_3^+$ ion given in the literature were as follows: from allene 284, propylene 280, 2-butene 287, isobutene 290 and cyclopropane 286 kcal./mole. Since from allene the reaction

$$CH_2{=}C{=}CH_2 + e \longrightarrow CH_2{=}C{=}\overset{+}{C}H + H + 2e \qquad (7)$$

seemed to be the most straightforward process for the formation of $C_3H_3^+$, and since the values of $\Delta H_f(C_3H_3^+)$ from the other molecules were almost the same, Field made the quite reasonable assumption that the $C_3H_3^+$ ion had the allenyl ($CH_2{=}C{=}\overset{+}{C}H$) structure in all cases. We feel, however, that the apparent agreement of the data from the literature is misleading. For instance, the appearance potential of $C_3H_3^+$ from allene, measured by Delfosse and Bleakney,[5] was 12.5 ± 0.2 v. We carefully redetermined this appearance potential and obtained a considerably lower value: 12.02 ± 0.03 v., which leads to $\Delta H_f(C_3H_3^+) = 271$ kcal./mole. In order to check the value of 280 kcal./mole for $\Delta H_f(C_3H_3^+)$ based on Delfosse and Bleakney's appearance potential in propylene we measured the ionization efficiency curve for this process. It was found that the curve had a very large tail and an evaluation of the appearance potential was quite indeterminate as can be seen by the disagreement between the values obtained by different methods of measurement: linear extrapolation 15.28 v., vanishing current 14.35 v.; and for the semi-log method 14.85 for the 1% value and 14.43 for the 0.1% value. Extrapo-

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(9) R. E. Fox and A. Langer, *J. Chem. Phys.*, **18**, 460 (1950).

(10) F. D. Rossini, *et al.*, Selected Values, etc., Circular 500, National Bureau of Standards 1952.

(11) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press 1953.

lation of the ΔV line gave 14.26 v. These results show that the curvature is so great that the appearance potential is in doubt to about 0.5 v. (11–12 kcal./mole). It may be noted that Dibeler's quoted values from the 2-butenes[12] were given with an estimated uncertainty of 7 kcal./mole, and Stevenson and Hipple's value from isobutene[13] was given with an uncertainty of 11–12 kcal./mole. These estimated uncertainties are much larger than those given for other ions listed in the same papers, suggesting that these curves may similarly have had long tails which made the measurements difficult. This was found to be the case for *cis*- and *trans*-2-butene in the present work.

In Table III is given a summary of the values of $\Delta H_f(C_3H_3^+)$ calculated from the appearance potentials measured in this work and from those given in the papers quoted above. The results of a recent study of the appearance potentials of $C_3H_3^+$ ions in substituted acetylenes by Coats and Anderson[2b] are also included. Inspection of the values shows that they fall into two sets which do not overlap. For the sake of clarity the values belonging to the lower set (257–271 kcal./mole) are listed in column 1 and those in the higher set (280–293 kcal./mole) in column 2. The values derived from appearance potentials for which large limits of error are reported, or from ionization efficiency curves known from the present work to have long tails, have been placed in brackets. It is immediately obvious that all the bracketted values belong in the higher set. It would appear that this set of values corresponds either to the formation of a different species of $C_3H_3^+$ ion from that produced in the lower set, or to the production of the same $C_3H_3^+$ ion ($\Delta H_f \sim 265$ kcal./mole) but having kinetic or excitational energy of 20–25 kcal. In view of the prevalence of tailed curves in the higher set, the latter alternative appears quite probable, except possibly for cyclopropane.

TABLE III

VALUES OF THE HEAT OF FORMATION OF $C_3H_3^+$ ION

Compound	$\Delta H f(C_3H_3^+)$ This work 1	2	Lit. 1	2
Allene	271			[282][5]
1,2-Butadiene	260			
1,3-Butadiene	264		270[9]	
Propyne	269		264[2b]	
1-Butyne	263		257[2b]	
2-Butyne			269[2b]	
Propylene		[285]		[280][5]
1-Butene		[286]		[282][12]
2-Butene-*cis*		[286]		[285][12]
2-Butene-*trans*		[290]		[293][12]
Isobutene				[291][13]
Cyclopropane				286[2a]

Coats and Anderson calculated from their data that $\Delta H_f(C_3H_3^+) = 256$ kcal./mole, and to this ion they assigned the propargyl structure. Using group contributions they calculated $\Delta H_f(CH_3{-}C{\equiv}C^+)$ to be about 383 kcal./mole, $\Delta H_f(CH_2{=}C{=}C^+H)$ to be about 351 kcal./mole while that of $C^+H_2{-}C{\equiv}CH$ was only 256 kcal./mole. Although such calculations are necessarily only approximate, their conclusion that $C_3H_3^+$ ion is the propargyl ion appears to be well founded. Additional evidence for the propargyl form can be drawn from the results of a recent investigation of the mercury photosensitized decomposition of allene, 1,2-butadiene and 1,3-butadiene,[14] in which it has been shown that the reaction of allene proceeds by the removal of a H atom to form a C_3H_3 radical. The reaction of this radical with added methyl radicals resulted in the formation of 1-butyne rather than 1,2-butadiene, showing that the radical had a structure closer to the propargyl configuration than to the allenyl configuration, the latter having consequently the lesser stability. The same radical was produced from the butadienes. Unless the relative stabilities are reversed in the ionic structures, which seems unlikely in view of Coats and Anderson's calculation mentioned above, it is reasonable to suppose that the dissociation of these compounds by electron impact is analogous to that brought about by collision with excited Hg atoms, and leads to formation of an ion having a structure closer to that of propargyl ion. On account of the large difference in the heats of formation of the two ionic forms, there may be little or no resonance hybridization in the ionic form, and the actual structure may be very close to the propargyl one.

(3) **The Heat of Formation of the C_3H_3 Ion and Radical.**—The data given in Table III suggest that the heat of formation of the $C_3H_3^+$ ion, which we may provisionally identify as the propargyl ion, has a value between 265 and 270 kcal./mole. The average of the values given in column 1, including Coats and Anderson's data, is 265 kcal./mole. The heat of formation of the propargyl radical may then be calculated using the ionization potential of the propargyl radical (8.25 ± 0.08 v.) measured directly by electron impact on propargyl radicals.[15] This gives $\Delta H_f(C_3H_3) = 75$ kcal./mole.

(4) **Bond Dissociation Energies.**—There are two ways of obtaining bond dissociation energy values from the present data. One is by using the relation

$$D(C_3H_3\text{-}X) \lessdot A(C_3H_3^+) - I(C_3H_3)$$

for each appearance potential. The second way is to use the average value derived above, $\Delta H(C_3H_3) = 75$ kcal./mole, and the relation

$$D(C_3H_3\text{-}X) = \Delta H_f(C_3H_3) + \Delta H_f(X) - \Delta H_f(C_3H_3X)$$

The latter method is to be preferred on the basis of greater consistency and the bond dissociation data given in Table IV were calculated in this way.

TABLE IV

VALUES OF C–H AND C–C BOND DISSOCIATION ENERGIES

Compound	Bond	Dissociation energy This work	Coats and Anderson[2b]
Allene	$H{-}C_3H_3$	81.2	..
Propyne	$H{-}C_3H_3$	82.8	82
1,2-Butadiene	$CH_3{-}C_3H_3$	68.2	..
1-Butyne	$CH_3{-}C_3H_3$	67.5	59

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[12] V. H. Dibeler, *J. Research Natl. Bur. Standards*, **38**, 329 (1947).

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

[14] J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).

[15] J. B. Farmer and F. P. Lossing, *ibid.*, **33**, 861 (1955).

(a) **Allene and Propyne.**—It is interesting to consider the meaning of the C–H bond dissociation energy value in allene and propyne. The corresponding bond rupture processes in the allene and propyne molecules are, respectively

$$CH_2{=}C{=}CH_2 \longrightarrow CH_2{=}C{=}\dot{C}H + H \tag{8}$$

$$D(CH_2{=}C{=}CH{-}H) = \Delta H_f(\dot{C}H_2{=}C{=}CH) + \Delta H_f(H) - \Delta H_f(\text{allene})$$

$$CH{\equiv}C{-}CH_3 \longrightarrow CH{\equiv}C{-}\dot{C}H_2 + H \tag{9}$$

$$D(CH{\equiv}C{-}CH_2{-}H) = \Delta H_f(CH{\equiv}C{-}\dot{C}H_2) + \Delta H_f(H) - \Delta H_f(\text{propyne})$$

At first sight one might expect the C–H bond in allene to be considerably stronger than in propyne since it appears to be an ethylenic hydrogen and, in fact, the bond *energy* may be greater. However, as mentioned above, it has been shown[14] that the loss of a **H** atom from allene results in the formation of a C_3H_3 radical which has a propargyl configuration rather than an allenyl one and that the forms $CH{\equiv}C{-}\dot{C}H_2$ and $\dot{C}H{=}C{=}CH_2$ are probably resonance hybrids. If this is indeed the case then the same radical is formed by removing a H-atom from allene as by removing a H atom from the methyl group in propyne. The terms $\Delta H_f(CH_2{=}C{=}\dot{C}H)$ and $\Delta H_f(CH{\equiv}C{-}\dot{C}H_2)$ in reactions 8 and 9 are therefore identical. Since the heats of formation of allene and propyne differ only by 1.6 kcal./mole[11] the bond dissociation energies are consequently the same within this limit. The observation, from the present work, that $A(C_3H_3^+)$ from allene = $A(C_3H_3^+)$ from propyne (Table II) can be interpreted in only two ways: either the allene and propyne molecule ions rearrange to a common form before dissociation, in which case the two C–H bond dissociation energies correspond in fact to the same process, or the loss of a H-atom from allene ion forms a propargyl ion and the C–H bond dissociation energies are actually the same for both allene and propyne. In the former case a hydrogen shift must occur in the allene molecule ion with almost zero activation energy. In the latter case the "rearrangement" shown in reaction 10 must occur at the moment of dissociation with almost zero activation energy for the ion as well as the radical

$$\dot{C}H{=}C{=}CH_2 \longrightarrow CH{\equiv}C{-}\dot{C}H_2 \tag{10}$$

The value of $D(C_3H_3{-}H)$ = 82 kcal./mole for allene and propyne is surprisingly low for a C–H bond and is in fact only slightly higher than the C–H bond in propylene, for which $D(\text{allyl-H}) \sim 79$ kcal./mole.[16] This supports the conclusion reached above that resonance is permitted to the C_3H_3 radical, although not so extensively as to the allyl radical, in which the resonating structures are of identical form.

(b) **1,2-Butadiene and 1-Butyne.**—The discussion given above for the C_3H_3–H bonds in allene and propyne applies with equal force to the C_3H_3–CH_3 bonds in 1,2-butadiene and 1-butyne. The corresponding bond rupture processes in the C_4 molecules are

$$CH_2{=}C{=}CH{-}CH_3 \longrightarrow CH_2{=}C{=}\dot{C}H + CH_3 \tag{11}$$

$$D(CH_2{=}C{=}CH{-}CH_3) = \Delta H_f(CH_2{=}C{=}\dot{C}H) + \Delta H_f(CH_3) - \Delta H_f(\text{1,2-butadiene})$$

$$CH{\equiv}C{-}CH_2{-}CH_3 \longrightarrow CH{\equiv}C{-}\dot{C}H_2 + CH_3 \tag{12}$$

$$D(CH{\equiv}C{-}CH_2{-}CH_3) = \Delta H_f(CH{\equiv}C{-}\dot{C}H_2) + \Delta H_f(CH_3) - \Delta H_f(\text{1-butyne})$$

Since the C_3H_3 radicals formed in reactions 11 and 12 are effectively the same, the dissociation energies of the C_3H_3–CH_3 bonds in 1,2-butadiene and 1-butyne should differ only by the difference in ΔH_f for 1,2-butadiene and 1-butyne. This difference is only 0.7 kcal./mole,[11] and $D(C_3H_3{-}CH_3)$ in both molecules is consequently ~68 kcal. As can be seen from Table IV, this value is about 9 kcal. higher than that found by Coats and Anderson, whose appearance potential of $C_3H_3^+$ from 1-butyne gave a value for $\Delta H_f(C_3H_3^+)$ appreciably below the average of their other data. The appearance potential from 1-butyne found in this work was consistent with the average of $\Delta H_f(C_3H_3^+)$ = 265 kcal./mole, and was identical with $A(C_3H_3^+)$ from 1,2-butadiene. The same argument as for allene and propyne given above applies to this electron impact dissociation; either the 1,2-butadiene and 1-butyne rearrange to a common form and then dissociate, or the $C_3H_3^+$ ion and the C–CH_3 bond dissociation energy are the same in both. The latter is the preferred interpretation.

The appearance potential of the CH_3^+ ion from 1,2-butadiene is also listed in Table II. From this value, 14.4 ± 0.2 v. and the ionization potential of CH_3 radical, 9.95 v.[17] $D(C_3H_3{-}CH_3)$ = 103 kcal./mole, a value that is evidently much too high. There seems no doubt that the formation of the CH_3^+ ion is accompanied by 35–40 kcal. of kinetic or excitational energy.

(c) **1,3-Butadiene and 2-Butyne.**—It was noted earlier that a shift of a hydrogen atom in the ion, needing little or no activation energy, was required to explain the consistency of the value of $\Delta H_f(C_3H_3^+)$ from 1,3-butadiene with the other data in Table III. An even more extensive shift is required to explain Coats and Anderson's value of $\Delta H_f(C_3H_3^+)$ = 269 kcal./mole from 2-butyne. The process corresponding to this energy is

$$CH_3{-}C{\equiv}C{-}CH_3 + e \longrightarrow (\overset{+}{C}H_2{-}C{\equiv}CH) + CH_3 + 2e$$

$$A(C_3H_3^+) = \Delta H_f(C_3H_3^+) + \Delta H_f(CH_3) - \Delta H_f(\text{2-butyne}) \tag{13}$$

The alternative $C_3H_3^+$ ion, $CH_3{-}C{\equiv}C^+$, which would be formed by the straightforward rupture of the C—CH_3 bond was calculated by Coats and Anderson to have a much higher heat of formation. In view of this shift, it is debatable whether the value of $D(CH_3{-}C{\equiv}C{-}CH_3)$ = 73 kcal./mole derived from this data by Coats and Anderson should not rather have been assigned to the C_3H_3—CH_3 bond in 1-butyne or 1,2-butadiene.

The appearance potential of $C_2H_3^+$ from 1,3-

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[16] C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1956).

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

butadiene was found to be 15.72 ± 0.08. Assuming the process to be

$$CH_2{=}CH{-}CH{=}CH_2 + e \longrightarrow C_2H_3^+ + C_2H_3 + 2e \quad (14)$$

then $A(C_2H_3^+) = \Delta H_f(C_2H_3^+) + \Delta H_f(C_2H_3) - \Delta H_f$(1,3-butadiene). Using Field's value of $\Delta H_f(C_2H_3) = 82$ kcal./mole,[18] this appearance potential gives $\Delta H_f(C_2H_3^+) = 307$ kcal./mole, a value considerably higher than the average of 281 kcal./mole obtained by Field from a number of compounds. Evidently this dissociation process involves some 26 kcal. of kinetic or excitational energy.

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(18) F. H. Field, *J. Chem. Phys.*, **21**, 1506 (1953).

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Isoprene Polymerization by Organometallic Compounds. I

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Organometallic compounds of lithium, sodium and potassium were used to initiate the polymerization of isoprene in various solvents. The effects of temperature, solvent, organic moiety and metallic ion on the structure of the polymer are reported. The controlling factors are the solvent and the nature of the positive counterion. For example, with *n*-butyllithium and heptane, over 90% *cis*-1,4-structure is obtained; with *n*-butyllithium or phenyllithium in tetrahydrofuran practically no 1,4-structure appears in the polymer; sodium and potassium compounds give quite different structures.

Introduction

In a previous publication (Hsieh and Tobolsky(1)) it was shown that in hydrocarbon solutions (benzene or heptane) of isoprene, *n*-butyllithium produced a polymer which had more than 90% *cis*-1,4-structure. In diethyl ether solutions of isoprene, butyllithium produced a polymer which had approximately 60% 3,4-structure, 10% 1,2-structure and 30% *trans*-1,4-structure. The most striking difference between these polymerizations was that under our conditions a precipitate was always present during the polymerization in hydrocarbon solutions, while the ether solutions appeared homogeneous during polymerization and showed little or no Tyndall effect. This work in no way proves that stereospecific polymerization could not occur under homogeneous conditions, but it did not in our experiments.

In this present work isoprene was polymerized by various organometallic compounds and in various solvents mostly under homogeneous conditions. It was our desire to evaluate the effect of temperature, solvent, organic moiety and positive counterion on the structure of the polymer.

Experimental

Material.—The organometallic compounds were synthesized and analyzed according to the procedure described by Gilman.(2) Phillips 99 mole % isoprene was redistilled under nitrogen before use. The solvents were carefully purified by well-known methods.

Polymerization.—The polyisoprenes were prepared by the evacuated sealed tube technique or in 2-ounce bottles with caps having self-sealing gaskets through which the reagents were injected by means of syringe needles. Manipulations with the reagents were conducted in a dry box and in an atmosphere of purified nitrogen.

The concentration of the catalysts used was 1 mole % with respect to the weight of isoprene. The volume of the solvent was 2.5 times that of the monomer. Polymerizations were allowed to proceed to at least 80% conversion. Light scattering properties of the reaction mixtures strongly suggested homogeneous polymerization. However, as polymerization approached 100% conversion, the reaction mixture darkened markedly so that possible Tyndall effects were obscured.

The polymers were isolated by slowly pouring the reaction mixture into methanol containing α-naphthylamine. Purifications were undertaken by repeated solution in benzene and precipitation with methanol. The purified polyisoprenes finally were dried *in vacuo* and 1% carbon disulfide solutions were prepared and studied by spectral analysis as described by Richardson.(3) The percentages of 1,2 *versus* 3,4- and 1,4-structures are probably valid within 3%; the relative amount of *cis*-1,4 *versus trans*-1,4 is valid to about 10%. The polymers ranged from sticky semi-liquids to rubbery solids. Viscosity measurements of the toluene solutions gave molecular weights of from 2000 to 15,000 according to published equations relating intrinsic viscosity and molecular weight.(4)

Results and Discussion

Anionic polymerizations (in homogeneous media) proceed by the following steps. First, the anionic initiator MR dissociates into M^+ and R^-. The anionic moiety R^- adds to the monomer (isoprene) to start a growing polymer chain. The propagating end of the chain is the ion pair (∼-isoprene$^-$ M^+). It is this ion pair that determines the structure of the polymer, because obviously the entering monomer is strongly influenced by the electrical and steric forces of the ion pair as it insinuates itself between the isoprene$^-$ and the M^+.

Inasmuch as the solvent may thoroughly solvate or even complex one or both members of the ion pair, one might expect that both the positive counterion and the solvent would have a very important influence on the structure of the polymer in homogeneous systems.

On the other hand, one should expect that the initiating moiety R^- would have much less influence on the structure of the polymer formed in homogeneous systems. Similarly, one might anticipate that the influence of temperature should not be major: higher temperatures might favor a somewhat more random structure.

The extent to which these predictions are borne out is shown in the tables.

Table I shows the major effects produced in the structure when the positive counterion and the solvent are varied. Column 1 gives the initiator; column 2 gives the solvent; column 3, the temper-

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(1) H. Hsieh and A. V. Tobolsky, *J. Polymer Sci.*, **25**, 245 (1957).

(2) H. Gilman, *et al.*, THIS JOURNAL, **54**, 1957 (1932); **62**, 1514 (1940).

(3) A. Richardson and W. Sacher, *J. Polymer Sci.*, **14**, 353 (1953).

(4) W. C. Carter, R. L. Scott and M. Magat, THIS JOURNAL, **68**, 1840 (1946).