the coefficient A_n being a known but complicated function of the index n and the concentration, and z_1 and z_2 being the *algebraic* valences of the cation and anion, respectively. In the present paper, we have used only the first-order term ($n = 1$) of this series: the justification for this was given in reference (1). The second-order term ($n = 2$) is proportional to

$$\frac{(z_1{}^2 - z_2{}^2)^2}{\bar{d}^2(z_1 - z_2)}\,(\kappa a)^2\left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^2 Ei(2\kappa a)$$

Now for values of (κa) small compared to unity, $Ei(2\kappa a)$ is proportional to $\log c$, and $(\kappa a)^2\left(\dfrac{e^{\kappa a}}{1 + \kappa a}\right)^2$ is proportional to c, so that the term in $c \log c$ arises

from this second-order electrophoretic correction at low concentrations. However, *for a symmetrical electrolyte* the valence-factor $(z_1{}^2 - z_2{}^2)^2/(z_1 - z_2)$ vanishes identically in the second-order term (and indeed in all even-order terms); hence there can be no term in $c \log c$ in the conductance equation in this case. Such a term is, however, possibly justifiable for unsymmetrical valence-type electrolytes, and certainly appears in the *diffusion* coefficient for the symmetrical case.[1a]

We are indebted to Dr. J. N. Agar of the University of Cambridge for drawing our attention to Falkenhagen's treatment[2] of the relaxation effect.

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The Ionization Potentials of Substituted Acetylenes by Electron Impact

BY J. L. FRANKLIN AND F. H. FIELD

The ionization potentials of acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 3-methyl-1-butyne, vinylacetylene and diacetylene were determined by the electron impact method. The values obtained (in e.v.) are 11.46, 10.48, 10.34, 9.85, 10.39, 10.35, 9.90 and *ca.* 10.9. The value for propyne is in serious diagreement with that obtained spectroscopically (11.30 e.v.). Possible sources for this discrepancy are discussed.

In the course of some electron impact studies being carried on in this Laboratory, we attempted to check the performance of our instrument by measuring the ionization potential of propyne, the value of which had presumably been well-established at 11.30 e.v. by the spectroscopic measurements of Price and Walsh.[1] Much to our surprise, we obtained almost a volt lower than this, and since we doubted that our instrument could be that much in error, we became somewhat suspicious of the published value. Since the only compounds in the acetylene series for which ionization potentials have been measured are acetylene itself, propyne and diacetylene, we decided to make the study described here. The compounds investigated were acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 3-methyl-1-butyne and vinylacetylene.

Experimental

The measurements were made using the apparatus and technique which has been described previously.[2] The vanishing current method was used in determining threshold voltages, and the electron voltage-scale calibrating gas (Kr) was introduced into the apparatus along with the gases under investigation. The temperature of the ion source was maintained at 190 $\pm$ 10° for all measurements except those on vinylacetylene, for which compound, because of its instability, no external heat was applied to the ion source. Under these conditions the ion source temperature was 100 $\pm$ 10° as a result of heating by the filament. A reproduction of the ionization efficiency curves for acetylene and propyne is given in Fig. 1.

Commercial acetylene was purified from acetone by freezing with Dry Ice. Its mass spectrum showed no peaks which could not be assigned to acetylene. The propyne was made by the Farchan Research Laboratories, Cleveland, Ohio, and was kindly supplied us by Mr. George Toups of these laboratories. The only really objectionable impurity

that it could contain would be its isomer, allene, which, because of its quite low ionization potential (10.19 e.v. by ultraviolet spectroscopy[3]; 10.0 e.v. by electron impact[4]), could lead to erroneously low results if present in the propyne to any significant extent. The mass spectrum of the propyne sample was obtained and showed no extraneous peaks, but it could not be used to detect the presence of allene impurity. Consequently, the infrared spectrum of the sample was very kindly obtained for us by Dr. S. H. Hastings of these laboratories, and from the essential absence of the characteristic bands to be ascribed to 1,2-diolefins, it was estimated that the allene content of the sample was less than 0.07%, surely a negligible amount. The 1-butyne and 2-butyne were N.B.S. Standard Samples with purities of 99.87 and 99.93 mole per cent. The pentynes were obtained from Shell Development Company, and were submitted to infrared analysis, which showed the 1,2-diolefin content to be of the order of 1%. The vinylacetylene was made by the du Pont Company of Louisville, Kentucky, and was used without further treatment. Its mass spectrum indicated that no significant impurities were present.

Results

The results of this study are listed in the second column of Table I. The uncertainties given are the average deviations from average for the five replicate determinations made on each substance. These five measurements were not done consecutively but rather were spaced out over the whole course of the work. It is felt that in this way the effect of short term peculiarities in the operation of the mass spectrometer is minimized and that the replicate determinations constitute individual measurements to a greater extent than would be the case were the determinations done consecutively. Since the ionization potential of acetylene is well-established, measurements on this compound were made mostly as a check on the accuracy of the apparatus and technique. The good agreement of

(1) W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 381 (1945).

(2) F. H. Field, *Rev. Sci. Instruments*, submitted for publication.

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

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

our value (11.46 e.v.) with Honig's[5] electron impact value of 11.43 e.v. and with Price's[6] spectroscopic value of 11.40 e.v. indicates that the results obtained from the apparatus are trustworthy. The difference of 0.03 e.v. between our results and Honig's results is trivial, and the fact that the electron impact results are higher than the spectrosopic results is, of course, quite typical.

TABLE I

IONIZATION POTENTIALS OF ACETYLENES

	Experimental ionization or appearance potential, volts	Calcd.[a] I_p, volts
Acetylene	11.46 ± 0.01	(11.46)
Propyne	10.48 ± .06	(10.68)
Butyne-2	9.85 ± .07	9.86
Butyne-1	10.34 ± .01	10.25
Pentyne-1	10.39 ± .01	10.17
3-Methyl-1-butyne	10.35 ± .03	10.00
Vinylacetylene	9.90 ± .09	.....
$C_4H_4 \rightarrow C_4H_2^+ + H_2$	12.88 ± .14	.....

[a] The potential parameters used were 11.46 and 13.31, respectively, the ionization potential of acetylene and the adjusted ionization potential of methane. The interaction of two alkyl groups was taken as 1.55 v. and that of alkyl with —C≡C— as 1.66 v.

It will be observed from Table I that methyl substitution brings about a marked lowering of the ionization potential, but that higher single alkyl substitution has little effect beyond that of methyl. In particular, the ionization potentials of propyne and of 2-butyne are, respectively, 1.0 and 1.6 v. lower than that of acetylene itself. As we mentioned previously, our results on propyne are in serious disagreement with the spectroscopic value of 11.30 e.v. obtained by Price and Walsh,[1] and this disagreement is all the more interesting because of the fact that in general, electron impact values tend to be higher than spectroscopic values.

In considering this disagreement further, it is first of interest to raise the question as to whether the electron impact ionization potentials of the alkyl substituted acetylenes are internally consistent. To do this, we have calculated the ionization potentials of the alkyl acetylenes above propyne by means of the method of group orbitals.[7,8] In these calculations, the interaction between an alkyl group and the ethinyl group is obtained from the observed ionization potential of acetylene and propyne, following which the effects of more extensive substitution can be obtained from the calculational formalism. The values so calculated are listed in column 3 of Table I, and the agreement with the experimental values is reasonably satisfactory, although it must be admitted that the downward trend with increasing single alkyl substitution is more marked in the calculated values than in the experimental values. However, the agreement in the case of 2-butyne, which is the most critical and significant test, is excellent. It has been shown by one of us[8] that such group orbital calculations give accurate results for quite a number of other classes of compounds; con-

(5) R. E. Honig, J. Chem. Phys., 16, 105 (1948).
(6) W. C. Price, Phys. Rev., 47, 444 (1935).
(7) G. G. Hall, Trans. Faraday Soc., 49, 113 (1953).
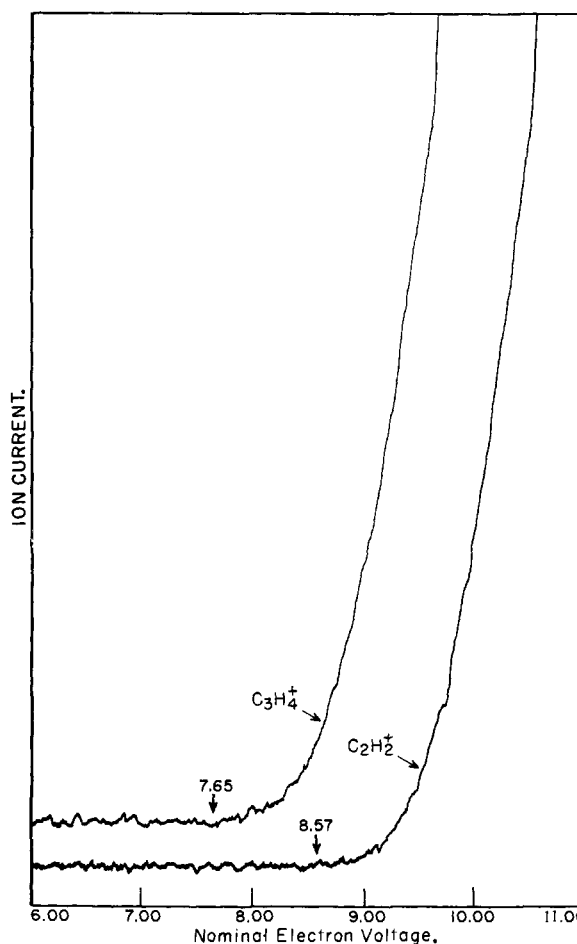(8) J. L. Franklin, J. Chem. Phys., to be published.

Fig. 1.—Ionization efficiency curves for acetylene and propyne. Arrows indicate threshold voltages. Base lines of curves displaced for sake of clarity.

sequently, the agreement here shows that our values for acetylene and the alkyl-substituted acetylenes are indeed internally consistent. On the other hand, if the calculations were made using Price and Walsh's[1] value to obtain the alkyl–ethinyl interaction, the calculated values for the other alkyl acetylenes would be very much higher. Thus, in essence, if Price and Walsh's value for propyne be correct, our values for all the alkyl acetylenes are incorrect, and, naturally, we tend to disbelieve this.

Furthermore, the trend of ionization potentials that we observed is more in accordance with that observed with other series of compounds than the trend implied by Price and Walsh's values. Thus, in the ethylene series, the ionization potentials[5] are 10.62, 9.84, 9.76, 9.66 and 9.30 for the compounds C_2H_4, C_3H_6, 1-C_4H_8, 1-C_5H_{10} and 2-C_4H_8, respectively. From this it is clear that alkyl groups interact strongly with the vinyl group, and our results imply about the same size interaction with the ethinyl group. Similarly, two vinyl groups interact strongly (ionization potential butadiene[9] = 9.24 e.v., i.e., a lowering of 1.4 e.v. in going from C_2H_4 to butadiene), and from our results, so do the vinyl group and the ethinyl group

(9) J. D. Morrison and A. J. C. Nicholson, ibid., 20, 1021 (1952).

(ionization potential of vinyl acetylene = 9.90 e.v., i.e., a lowering of 1.5 e.v. in going from C_2H_2 to vinyl acetylene).

We see no reason to expect markedly different interaction tendencies of the ethinyl and vinyl groups. It is true that in all likelihood the π-electrons are bound more firmly in the ethinyl group because of the shorter carbon–carbon bond distance, and as evidence we need only observe the much higher ionization potential of acetylene as compared with that of ethylene. However, we doubt that the tightness of the binding is so large as to give the extremely small interaction implied by Price and Walsh's ionization potential of propyne, and we think that our values are much more to be expected.

The next step to be taken in search for a source of the discrepancy is to question Price and Walsh's value. However, an examination of their paper reveals no dubious procedures, and we doubt that simple experimental error on their part is the solution to the difficulty. The spectra on which they base their value contain well-defined bands which comprise two Rydberg series, both converging to the same ionization limit. Furthermore, in the same paper they report the ionization potential of diacetylene, and as we will show later, their result is in reasonably good agreement with a value which can be deduced from our work.

The third possibility for the discrepancy is that either Price and Walsh or ourselves have not actually measured the lowest ionization potential for propyne. It is of interest that the heat of formation of the $C_3H_4{}^+$ ion which results from our ionization potential of 10.46 e.v. is 285 kcal./mole, and it also happens that the heat of formation of the $C_3H_4{}^+$ ion from allene is quite close to this (281 from ultraviolet spectroscopy, 277 by electron impact). In view of the essential equality of these values, one can speculate that perhaps the ion produced from propyne by electron impact has the allene molecule-ion structure; that is, isomerization occurs. By contrast the Price and Walsh ionization potential for propyne corresponds to a $C_3H_4{}^+$ ion heat of formation of 304 kcal./mole, which implies the existence of a different structure.

However, we are inclined to doubt this postulate on a number of grounds. First, the mechanism involved in such an isomerization must be as follows: the propyne molecule is excited by electron impact to an energy level equivalent to a heat of formation value of 285 kcal./mole, following which the rearrangement of hydrogen from the methyl group to the other terminal carbon atom (which is a shift across an intervening carbon) occurs, and finally, the electron is ejected to form the ion by a sort of auto-ionization process. Now it is true that auto-ionization processes are known and that extensive rearrangement can occur under electron impact. However, such rearrangements are always thought to involve ionic species and furthermore, the equivalence of the heat of formation value calculated from the ionization potential of propyne with that assigned to the allene molecule-ion structure implies that any rearrangement of the propyne in the ionization process occurs with practi-

cally no activation energy. Particularly in view of the fact that the rearrangement here involves a neutral molecule, we are inclined to consider this lack of activation energy to be an argument against the occurrence of rearrangement.

The second argument against the occurrence of isomerization concerns the observed ionization potentials of 1-butyne and 2-butyne. If propyne isomerizes under electron impact because of the relatively low energy of the allene molecule-ion, we might expect to see evidence for an analogous isomerization of 1-butyne and 2-butyne, since these also have isomers (1,3-butadiene and 1,2-butadiene) which form relatively low energy ions. The heat of formation of the 1,3-butadiene molecule-ion is 239 kcal./mole, but our ionization potentials for 1-butyne and 2-butyne correspond to heat of formation values of 277 and 262 kcal./mole, respectively. Obviously, no isomerization to 1,3-butadiene molecule-ion occurs, in spite of the fact that the rearrangement could be accomplished in 2-butyne merely by shifting two hydrogens to neighboring carbon atoms. The considerations involving 1,2-butadiene molecule-ion are made uncertain by our lack of knowledge of the 1,2-butadiene ionization potential. However, without doubt the 1,2-butadiene molecule-ion heat of formation is appreciably below the 285 kcal./mole assigned to allene molecule-ion, and thus our results indicate that the isomerization of 1-butyne to 1,2-butadiene does not occur. No conclusions can be drawn about the 2-butyne behavior. The fact that 1-butyne does not isomerize, when coupled with the fact that the 1-butyne and 2-butyne ionization potentials are internally consistent with those of the other acetylenes studied, leads one to the belief that isomerization does not occur for any of the molecules.

As mentioned above, Price and Walsh measured the ionization potential of diacetylene, obtaining a value of 10.741 e.v. We measured the appearance potential of the mass 50 ion from vinylacetylene and obtained a value of 12.88 e.v. We assume the equation for the reaction producing this ion to be $C_4H_4 + e^- \rightarrow C_4H_2{}^+ + H_2 + 2e^-$, and we also assume the $C_4H_2{}^+$ ion to have the diacetylene structure. From the measured appearance potential we calculate a heat of formation value for the $C_4H_2{}^+$ ion of 363 kcal./mole, which when combined with the value of the heat of formation of diacetylene yields an ionization potential of 11.3 e.v. Here the heats of formation of both the vinylacetylene and the diacetylene were estimated with Franklin's[10] method of group equivalents, taking the values of 54 and 15 kcal./mole as the group equivalents for the —C≡CH and —CH=CH₂ groups, respectively, and assuming resonance energies of 3 and 6 kcal./mole, respectively, for vinylacetylene and diacetylene. The agreement of this calculated diacetylene ionization potential with that obtained experimentally by Price and Walsh is not very good, but it can be shown that when H_2 is split out across a double bond in a molecule-ion (as is the case here), an activation energy of about 10 kcal./mole is usually observed. Assuming such an activation energy to be present in the formation of the diacetylene

(10) J. L. Franklin, Ind. Eng. Chem., 41, 1070 (1949).

molecule ion from vinylacetylene, the appearance potential observed corresponds to a diacetylene ionization potential of about 10.9 e.v., which tends to corroborate Price and Walsh's value. Thus, we find ourselves in a position of agreeing with Price and Walsh for acetylene and diacetylene but strongly disagreeing for propyne.

It is apparent that we cannot definitely attribute the discrepancy between our work and that of Price and Walsh to any specific cause. However, there is one further observation which must be mentioned. The propyne heat of formation corresponding to Price and Walsh's ionization potential is 304 kcal./mole, and it is of interest that certain molecules decompose under electron impact to give a $C_3H_4{}^+$ ion with energies quite close to 304 kcal./mole. Thus, it is possible that there is a more or less well-de-

fined state at the energy corresponding to the Price and Walsh ionization potential, but our work would indicate that it is not the ground state. However, such a postulate is not without its flaws, because Price and Walsh observe that the form of the spectrum for propyne is very similar to that for acetylene, for which a value in essential agreement with the electron impact value is obtained. Similarly, good agreement is obtained in the case of diacetylene. It is difficult indeed to understand why the propyne should behave differently from the other two compounds and what the nature of its excited state might be. It would certainly be of interest to have spectroscopic measurements made of the ionization potentials of the substituted acetylenes above propyne.

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Observations on Thermal Explosions of Diborane–Oxygen Mixtures[1]

By Alfred T. Whatley and Robert N. Pease

Diborane–oxygen mixtures explode after an induction period within a range of concentrations at 105° to 165°. Since slow decomposition of diborane is occurring simultaneously at these temperatures, a pyrolysis product—perhaps pentaborane—may be the normal sensitizing agent. Both hydrogen and ethylene narrow the explosion limits.

It has recently been shown[2] that the decomposition of diborane (B_2H_6) takes place slowly in the neighborhood of 100° by a series of quasi-reversible reactions yielding higher boranes and hydrogen. The relation between this process and the reaction of diborane with oxygen is a matter of some interest. Over-all oxidation should be a highly energetic process

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3(s) + 3H_2O(g):$$
$$\Delta H^\circ_{298} = -482.9 \text{ kcal.}[3]$$
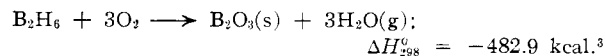
Nevertheless, Stock[4] reports no noticeable reaction with dry air or oxygen (presumably at room temperature), though explosion is said to have followed spillage of liquid diborane when the container was broken.

More recent work by Price[5] indicates that explosion does occur within a range of composition and pressure, though only at temperatures at or above those corresponding to slow decomposition.

The latter strongly suggests some interaction with the decomposition process, but no mention is made of anything in the way of an induction period or of an oxygen-sensitized decomposition of diborane. Price determined lower explosion limits by slowly bleeding pre-mixed gases into a clean reaction bulb until explosion occurred. Upper limits were observed by filling the cold reaction bulb to a higher pressure, bringing the thermostated bath up around the bulb, and then slowly evacuating after 1.5 minutes. In some cases, a third limit was also found by increasing the pressure instead of decreasing it as in second limit determinations. Lower limits were located over a range from about 135° to 225° for mixtures containing up to $33^1/_3\%$ diborane, but no limits could be found for 50% or richer mixtures. Upper limits were located a little above lower limits down to 165°, but at lower temperatures the method gave "upper limits" which actually lay below the "lower limits." There is further mention of an experiment on crossed streams of diborane and oxygen (presumably at one atmosphere), in which spontaneous ignition occurred when the temperature was raised to 132°.

Our interest in the diborane–oxygen interaction evolved from our earlier studies of the decomposition reaction.[2] It had been surmised that oxygen would sensitize diborane decomposition as it is known to do in the case of acetaldehyde, for example.[6] This expectation was based on the assumption that diborane (or the BH_3 radical) being electron-deficient would combine with the virtually unpaired electrons of oxygen to produce a reactive intermediate. No such effect was observed. For

(1) Taken from a thesis submitted by Alfred T. Whatley in partial fulfillment of the requirements for the Ph.D. degree. The work described in this paper was jointly supported by Contract NOrd-7920 with the U. S. Naval Bureau of Ordnance as coördinated by the Applied Physics Laboratory, The John Hopkins University, and by Contract N6-ori-105 with the Office of Naval Research as coördinated by Project Squid, Princeton University. Project Squid itself is sponsored jointly by the Office of Naval Research, the Office of Scientific Research (Air Force) and the Office of Ordnance Research (Army). We wish also to acknowledge the assistance of Dean Hugh S. Taylor, who has general supervision of this project.

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