Science. The writer wishes to thank Dr. John R. Johnson not only for suggesting the investigation but also for helpful advice.

Summary

1. The reaction velocity of a series of acetylenic chlorides has been measured according to the method of Conant.

2. A definite alternation in reactivity has been observed.

3. The most active acetylenic chloride measured has a somewhat lower activity than the corresponding ethylenic compound.

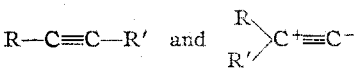
LYNCHBURG, VA. RECEIVED AUGUST 26, 1938

[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL LABORATORIES, LYNCHBURG COLLEGE]

Raman Spectra of Acetylenes. I. Derivatives of Phenylacetylene, $C_6H_5C{\equiv}CR$

BY M. J. MURRAY AND FORREST F. CLEVELAND

The Raman spectra of disubstituted acetylenes have been investigated by various workers, who have found that the characteristic acetylenic frequency in the region 2200–2300 cm.$^{-1}$ is usually double or triple, although in a few cases it is reported as a single, broad line.[1] Several explanations of this splitting have been given: Glockler and Davis[2] attribute the two strong lines in dimethylacetylene to symmetrical and asymmetrical vibrations. Gredy[3] suggests, as a working hypothesis, that two isomeric forms



$$R{-}C{\equiv}C{-}R' \quad \text{and} \quad {}^{R}_{R'}{>}C^{+}{\equiv}C^{-}$$

may exist simultaneously. Kohlrausch, Pongratz and Seka[4] regard the existence of two or more frequencies, if only one molecular form is present, as difficult to understand. Badger[5] attributes the doubling to a Fermi resonance interaction between the fundamental acetylenic frequency in this region and an overtone of a lower frequency near 700 or 1100 cm.$^{-1}$.

Gredy[3] found two lines for $C_6H_5C{\equiv}CCH_2OH$, while Faucounau[6] reported a single broad line for $C_6H_5C{\equiv}CCH_2CH_2OH$, and Bourguel and Daure[7] only a single frequency for $C_6H_5C{\equiv}CCl$. In view of these results and of the difference in opinion as to the cause of the splitting, it appeared worth while to investigate carefully the Raman spectra of disubstituted acetylenes in order to determine how the nature of the splitting varies for closely related molecules and to determine, if possible, whether there is a certain kind of substitution that yields only a single frequency. The present paper gives the results obtained for a series of compounds of the type $C_6H_5C{\equiv}CR$.

Experimental Procedure

The apparatus and experimental technique were essentially the same as previously described.[8] All the compounds were purified carefully by distillation in a heated column, using a high reflux ratio. Since the acetylenic compounds suffered photochemical decomposition when exposed to the exciting light and since the decomposition products were fluorescent and added greatly to the continuous background, it was necessary to redistill, from a flask attached to the scattering tube, at one-hour intervals during the exposures. In spite of these precautions, the continuous background was strong, especially in the case of the bromide.

The general procedure was to obtain several plates with both long and short exposure times, using both Hg 4047 Å. and 4358 Å. for excitation. The more intense lines could be measured with greater accuracy on the short exposure plates. In order to secure better definition of the stronger lines, the camera lens was stopped down to 5 mm. and a final exposure made. The time of this exposure was ten hours. The lines on these plates were exceedingly sharp and the acetylenic frequency in the 2200 cm.$^{-1}$ region, which on the other plates appeared as a single broad line, was resolved.

The comparator was illuminated with light from a yellowish-brown incandescent lamp, a practice which resulted in increased distinctness for the weaker lines.

Results

The results are given in the sections below, in which *k*, *f*, and *e* represent excitation by Hg 4047, 4347, and 4358 Å., respectively. Broad lines are designated by *b* and estimated intensities are given by the numbers in parentheses.

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(1) James H. Hibben, *Chem. Rev.*, **18**, 50-51 (1936).

(2) G. Glockler and H. W. Davis, *J. Chem. Phys.*, **2**, 881 (1934).

(3) Blanche Gredy, Thèses, Paris, 1935.

(4) K. W. F. Kohlrausch, A. Pongratz and R. Seka, *Sitzber. Akad. Wiss. Wien.*, Abt. IIb, **146**, 218 (1937).

(5) Richard M. Badger, *J. Chem. Phys.*, **5**, 178 (1937).

(6) Louis Faucounau, *Compt. rend.*, **199**, 605 (1934).

(7) M. Bourguel and P. Daure, *Bull. soc. chim.*, **47**, 1349 (1930); *Compt. rend.*, **190**, 1298 (1930).

(8) Forrest F. Cleveland and M. J. Murray, *Am. Phys. Teacher*, **5**, 270 (1937).

Brackets enclose those frequencies about which there is some question.

1. **3-Chloro-1-phenylpropyne-1** ($C_6H_5C\equiv CCH_2Cl$).—Synthesized by action of phosphorus trichloride on 3-phenyl-2-propynol-1 in the presence of pyridine and ether;[9] b. p. 99° (7 mm.); previous data, none.

Δν = 257(1)*e*. 272(1)*e*, 294($^1/_2$)*e*, 316(2)*e*, 333(2)*e*, 363(1)*e*. 379(3)*e*. 471(3)*k*, 529(3)*ke*, 612(2)*ke*. 630(2)*ke*, 690(6b)*ke*. 718(4)*ke*. 756(3)*ke*. 903(1)*ke*. 980(8)*kfe*, 1006(2)*ke*, 1030(1)*ke*, 1159(3)*ke*, 1174(3)*ke*, 1251(8)*ke*, 1275(3)*ke*, 1380(1)*ke*, 1423(3)*ke*, 1443(3)*ke*, 1471(1)*ke*, 1491(4)*ke*, 1530(1)*ke*. 1600(9)*ke*, 2214(10)*ke*. 2231(10)*ke*. 2263(4)*ke*. 2956(3)*e*. 2969(2)*ke*. 3046(2)*ke*. 3064(4)*ke*.

2. **4-Chloro-1-phenylbutyne-1** ($C_6H_5C\equiv CCH_2CH_2Cl$).—Synthesized by two methods: (a) by action of thionyl chloride upon 4-phenyl-3-butynol-1 in the presence of pyridine,[6] b. p. 107–108° (7 mm.); (b) by action of β-chloroethyl *p*-toluenesulfonate, 2 moles, on phenylacetylenemagnesium bromide;[10] b. p. 104° (5 mm.): both products gave the same spectra; previous data, Faucounau.[6]

Δν = 234(1)*ke*, 337(1)*ke*, 353(2)*ke*, 372(2)*ke*, 386(2)*ke*, 459(2b)*k*, 486(2b)*ke*, 520(4)*ke*, 535(4)*ke*, 550(1)*ke*, 624(3)*ke*, 646(3)*ke*. 665(4)*ke*, 700(3)*ke*, 754(5)*ke*, 912(1)*ke*, 987(2)*ke*, 1000(6)*ke*, 1032(3)*ke*, 1162(3)*ke*, 1181(3)*ke*, 1213(1)*ke*, 1244(5)*ke*, 1263(6)*ke*, [1329(1)*e*], 1424(3)*ke*, 1447(4)*ke*, 1491(4)*ke*, 1533(2)*ke*. 1603(9)*ke*, 2204(3)*ke*, 2221(10)*ke*. 2246(10)*ke*, 2293(2)*e*.2842(1)*e*, 2909(4)*e*.3010(1)*e*,3034(1)*e*, 3050(3)*ke*, 3063(5)*ke*.

3. **5-Chloro-1-phenylpentyne-1** ($C_6H_5C\equiv CCH_2CH_2CH_2Cl$).—Synthesized by action of γ-chloropropyl *p*-toluenesulfonate upon sodium phenylacetylide in di-*n*-butyl ether;[10] b. p. 125° (6 mm.); previous data, none.

Δν = 240(1)*ke*, 292(1)*e*, 373(3)*ke*, 408(1)*ke*, 440(3)*ke*, 521(3b)*ke*, 551(3)*ke*, 625(3)*ke*, 654(4)*ke*. 693(3)*ke*, 712(1)*ke*, 756(3)*ke*, 770(1)*ke*, 790(1)*ke*, 835(1)*ke*, 926(1)*ke*, 980(3)*ke*. 1000(7)*ke*, 1027(1)*ke*, 1062(1)*ke*, 1095(1)*ke*, 1154(3)*ke*, 1177(3)*ke*, 1241(4)*ke*, 1258(6)*ke*, 1276(2)*ke*, 1334(2)*ke*, 1435(4)*ke*, 1489(3)*ke*, 1528(1)*ke*, [1547(1)*ke*], 1580(2)*ke*, 1600(8)*ke*, 2220(10)*ke*, 2236(10)*ke*, 2900(3)*e*, 2923(3)*e*, 2956(2)*e*, 2984(2)*e*, 3049(3)*e*, 3063(5)*ke*.

4. **3-Bromo-1-phenylpropyne-1** ($C_6H_5C\equiv CCH_2Br$).—Synthesized by action of phosphorus tribromide upon 3-phenyl-2-propynol-1 in the presence of pyridine and ether;[11] b. p. 105–106° (5 mm.); previous data, none; continuous background very strong.

Δν = 287(1)*e*, 304(1)*e*, 374(2)*e*, 518(1)*e*, 530(1)*e*, 609(6b)*e*, 710(2)*e*, 757(1)*e*, 968(3)*e*, 987(6)*e*, 1023(1)*e*, 1155(1)*e*, 1169(1)*e*, 1186(4)*e*, 1206(5)*e*. 1269(3)*e*, 1476(3)*e*, 1489(3)*e*, 1599(8)*e*, 2204(3)*ke*, 2226(10)*ke*, 2265(4)*ke*, 3064(3)*ke*.

5. **3-Phenyl-2-propynol-1** ($C_6H_5C\equiv CCH_2OH$).—Synthesized by action of formaldehyde on phenylacetylenemagnesium bromide;[12] b. p. 112° (5 mm.): previous data, Gredy.[3]

Δν = [180(2)*e*], [195(2)*e*], 250(1b)*ke*, 270(2)*ke*, 282(2)*ke*, 302(1)*ke*, 336(1)*ke*, 350(2)*ke*, 366(3)*ke*, 382(4)*e*, 426(1)*ke*, 438(1)*ke*, 458(2b)*k*. 476(2b)*ke*, 512(2b)*ke*, 530(2)*ke*, 553(2)*ke*, 573(2)*ke*, 590(2)*ke*, 605(1)*ke*, 625(2b)*ke*. 648(1)*ke*, 663(1)*ke*, 703(1)*ke*, 721(2)*ke*, 743(3)*ke*. 761(3)*ke*, 789(2)*ke*, 956(3)*ke*. 985(2)*ke*, 1000(7)*ke*, 1028(3)*ke*, 1151(2)*ke*, 1164(4)*ke*, 1179(4)*ke*, 1238(4)*ke*, 1258(6)*ke*, 1285(1)*k*, 1331(1)*k*, 1439(3)*ke*, 1456(3)*ke*, 1496(3)*ke*. 1603(9)*ke*, 2202(3)*ke*, 2231(5)*ke*, 2242(10)*ke*, [2290(2)*e*], 2818(1)*ke*, 2951(2)*e*, 2978(1)*ke*, 3061(4)*ke*.

6. **4-Phenyl-3-butynol-1** ($C_6H_5C\equiv CCH_2CH_2OH$).—Synthesized by way of ethylene oxide on phenylacetylenemagnesium bromide;[13] b. p. 130° (7 mm.); previous data, Faucounau.[6]

Δν = 248(1)*ke*, [265(3)*k*], 386(2)*ke*, 405(1)*ke*, 510(2)*ke*, 528(3b)*ke*, 558(2b)*ke*, 609(2)*ke*, 624(3)*ke*, 700(3b)*ke*, 730(1)*ke*, 747(2)*ke*, 759(3)*ke*, 847(2)*ke*, 874(1)*ke*, 893(1)*ke*, 936(1)*ke*, 980(3)*ke*, 1000(7)*ke*, 1027(2)*ke*, 1162(3)*ke*, 1181(3)*ke*, 1241(5)*ke*, 1259(5)*ke*, 1288(1)*k*, 1308(1)*k*, 1329(1b)*ke*, 1374(1)*ke*, 1432(3)*ke*, 1440(3)*ke*, 1469(1)*k*, 1492(3b)*ke*, 1530(1)*ke*, 1602(9)*kfe*, 2214(4)*ke*, 2233(10)*ke*, 2895(2)*ke*, 2918(2)*ke*, [2935(2)*ke*], 3053(3)*ke*, 3070(3)*ke*.

7. **3-Chloro-1-phenylpropene-1 (Cinnamyl Chloride,** $C_6H_5CH{=}CHCH_2Cl$).—Eastman product, redistilled in column; b. p. 94° (5 mm.); previous data, none.

Δν = 248(2)*e*, 264(2)*e*, 302(2)*e*, 413(1)*ke*, 447(1)*ke*, 457($^1/_2$)*ke*, 507(2)*ke*, 605(4)*ke*, 619(3)*ke*, 670(5)*ke*, 678(4)*ke*, 699(3)*ke*, 746(1)*ke*, 814(2)*ke*, 823(1)*ke*, 849(3)*ke*, 915(2)*ke*, 924(2)*ke*, 963(1)*ke*, 1000(6)*ke*, 1033(2)*ke*, 1065(1)*ke*, 1080(2)*ke*, 1157(5)*ke*, 1184(3)*ke*, 1212(4)*ke*, 1251(7)*ke*, 1282(3)*ke*, 1303(4)*ke*, 1442(3b)*ke*, 1497(3)*ke*, 1538(1)*ke*, 1600(9)*ke*, 1660(10)*ke*, 2876(2b)*e*, [2944(1)*e*], 2967(2)*e* 3054(3)*e*, 3072(2)*e*.

Discussion of Results

The frequencies obtained agree quite well with those reported by Gredy[3] for $C_6H_5C\equiv CCH_2OH$ and with those reported by Faucounau[6] for $C_6H_5C\equiv CCH_2CH_2OH$ and for $C_6H_5C\equiv CCH_2CH_2Cl$, but the present results show many lines not listed by these earlier investigators. The compounds were prepared by essentially the same methods and were carefully purified. As a check upon the possibility that impurities might be the source of the additional lines, $C_6H_5C\equiv CCH_2CH_2Cl$ was prepared by a different method.[10] The resultant spectrograms were comparatively free from continuous background and showed not only the forty more prominent lines listed above but also forty-nine weaker ones which were quite generally checked by both Hg4047 Å. and 4358 Å.

It is possible that a few of these may be due to traces of impurities which were not removed by the careful fractionation, but the source of others cannot be laid to this as they occur in regions

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(9) M. J. Murray, This Journal, **60**, 2662 (1938).

(10) J. R. Johnson, A. M. Schwartz and T. L. Jacobs, *ibid.*, **60**, 1882 (1938).

(11) Tchao, Y. L., *Bull. soc. chim.*, [4] **53**, 1533 (1933).

(12) "Org. Syntheses," Coll. Vol. I, 1932, p. 182, by adaptation.

(13) Danehy, Vogt and Nieuwland, This Journal, **57**, 2327 (1935), reported a yield of 21% for this synthesis. However, by use of benzene as a diluent,[12] p. 299, and by allowing the rearrangement of the intermediate product to take place at 70–80°, yields of the alcohol approaching 70% were obtained in the present investigation.

where prominent lines are rare in organic compounds. Furthermore, a considerable number of the frequencies correspond to the weaker Raman lines in the spectra of benzene,[14] monosubstituted benzenes,[15] and compounds containing one or more —CH_2— groups. Because of certain remaining inconsistencies and difficulties in the measurement of the weaker lines, only the more prominent frequencies of the various compounds are listed at present.

The use of a low pressure mercury arc, with a consequent diminution in the amount of continuous radiation in the exciting light, and the method of illuminating the comparator are, without doubt, two of the factors contributing to the observance of so many lines. The number obtained is greater for some of the compounds than for others. This is due to the fact that some compounds decompose more readily when illuminated, resulting in the presence of small amounts of fluorescent materials. The consequent increase in the strength of the continuous background makes the measurement of weak lines extremely difficult.

Acknowledgment.—This work was aided in part by a grant from the Virginia Academy of Science from funds allotted it by the American Association for the Advancement of Science.

Summary

1. The principal lines in the Raman spectra of 3-chloro-1-phenylpropyne-1, 4-chloro-1-phenylbutyne-1, 5-chloro-1-phenylpentyne-1, 3-bromo-1-phenylpropyne-1, 3-phenyl-2-propynol-1, 4-phenyl-3-butynol-1, and 3-chloro-1-phenylpropene-1 (cinnamyl chloride) are reported.

2. Many other lines of very low intensity have been observed. Many of these are characteristic of benzene, monosubstituted benzenes, and compounds containing the —CH_2— group.

LYNCHBURG, VIRGINIA RECEIVED AUGUST 26, 1938

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[14] P. Grassmann and J. Weiler, *Z. Physik*, **86**, 321 (1933).

[15] J. W. Murray and D. H. Andrews, *J. Chem. Phys.*, **1**, 406 (1933); L. Kahovec and A. W. Reitz, *Akad. Wiss. Wien, Ber.*, **145**, 1045 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE WILLIAMS OIL-O-MATIC HEATING CORPORATION]

Hydrogen Bonds Involving the C–H Link. IV. The Effect of Solvent Association on Solubility

BY M. J. COPLEY, G. F. ZELLHOEFER AND C. S. MARVEL

In a series of papers,[1-3] by the authors, solubility data have been reported on a number of gaseous halogenated hydrocarbons (of the types CH_3X, CH_2X_2, CHX_3, CX_4, and C_2X_6) in a variety of solvents containing donor atoms (oxygen, nitrogen, and sulfur). The successive replacement of three of the hydrogen atoms of methane by halogen atoms results in each case in an increase of solubility, and for the type CHX_3 solubilities much in excess of the theoretical have been observed in many solvents; however, replacement of the fourth hydrogen produces an enormous drop in solubility compared to that shown by the haloform type. These results readily are interpreted by assuming that complex formation takes place through the bonding of a hydrogen atom of the halogenated hydrocarbon to an exposed pair of electrons on the nitrogen or oxygen atoms in solvent molecules. The presence of the strongly electron-attracting halogen atoms on the carbon activates the hydrogen atom and makes it available for coördination to the donor atom.

Latimer and Rodebush[4] first suggested the theory that a proton in certain cases is capable of forming a bond between two atoms. Since then numerous investigations have confirmed this theory and shown its great utility. The possibility that the hydrogen atom of a haloform molecule might be capable of forming such a bond to an oxygen or nitrogen atom in a molecule was proposed by Glasstone[5] to account for the dielectric behavior of binary mixtures, containing a haloform and either an ether, an ester, or an amine. The ease with which the large amount of solubility data[2] accumulated by the authors may be

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[1] G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).

[2] G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337 (1938).

[3] G. F. Zellhoefer and M. J. Copley, *ibid.*, **60**, 1343 (1938).

[4] Latimer and Rodebush, *ibid.*, **42**, 1419 (1920).

[5] Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937).