

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Hydrogen Bonding Studies. VI. The Hydrogen Bonding Properties of Acetylenes¹

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The relative acidity of terminal acetylenes as proton donors in hydrogen bond formation has been studied by measuring the shifts of the acetylenic C-H infrared stretching bands upon hydrogen bonding to reference bases. The relative basicity of acetylene has been studied similarly by measuring the shifts of the O-H stretching band of phenol upon hydrogen bonding to the acetylenes. The results are explained in terms of inductive and resonance effects. Examination of the C-H stretching band of terminal acetylenes as a function of concentration indicates that these compounds are weakly associated by intermolecular hydrogen bonding.

The marked solubility of acetylene in basic organic solvents² and the deviations from Raoult's law observed for such solutions^{3,4} have led many workers to postulate the existence of hydrogen bonds from the acetylenic proton to basic sites on the solvent molecules. The exothermic solution of phenylacetylene in ethers and amines has also been attributed to C-H hydrogen bonding.⁵ The first direct evidence for this type of hydrogen bonding was presented by Stanford and Gordy, who found that the acetylenic C-H stretching absorption band of phenylacetylene at 3315 cm.⁻¹ was shifted by 20-45 cm.⁻¹ to lower frequency in the presence of ethers and amines.⁶ Recently, similar C-H band shifts have been observed both for acetylene^{6,7} and for a number of substituted acetylenes.^{7,8} In addition, the C-H band shifts upon hydrogen bond formation have been used by Cook⁹ and by Baker and Harris¹⁰ as a measure of the relative basicity of carbonyl oxygen atoms.

The basic properties of the acetylenic triple bond toward hydrogen bond formation have received much less attention. Intramolecular hydrogen bonding of the hydroxyl group to the C-C triple bond has been reported to take place in *o*-ethynylphenol¹¹ and aliphatic acetylenic alcohols.¹² Intermolecular hydrogen bonding of phenol to 1-hexyne has been mentioned in a previous publication from these Laboratories.¹³

The present paper reports a more complete study by infrared spectroscopy of the relative Lewis acidities¹⁴ and basicities of a number of acetylenes

in hydrogen bond formation. Relative acidities of terminal acetylenes were measured by the shift of the acetylenic C-H band upon admixture with the reference bases N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF) and 1,2-dimethoxyethane (GDME). The C-H stretching band in some of the terminal acetylenes was also investigated as a function of the concentration of the acetylene in carbon tetrachloride, in order to examine the possibility of intermolecular association of terminal acetylenes by hydrogen bond formation. Relative basicities were measured by the shift of the O-H stretching band of the reference acid phenol upon hydrogen bonding to the acetylenes.

Experimental

Spectra.—The infrared spectra were all determined using a Perkin-Elmer Model 112 Spectrophotometer. A lithium fluoride prism calibrated with water, ammonia and carbon monoxide was used for the region 3700-2000 cm.⁻¹. The positions of sharp bands were reproducible to within ± 1 cm.⁻¹.

In the studies of acetylene basicity, phenol was present at 0.02 *M*, and acetylene concentrations were 1 *M* for alkynes, 1.6 *M* for diphenylacetylene and 2 *M* for other acetylenes. A path length of 3 mm. was used. In the studies of hydrogen bonding acidity, the bases (DMA, DMF and GDME) were present at 2 *M*. With DMA and GDME, the acetylenes were studied at 0.6 to 0.8 *M* and 0.1 mm. path length; with DMF, the acetylene concentration was 0.06 to 0.07 *M*, and the path length was 1 mm.

The positions of hydrogen-bonded bands were determined in the following manner: A spectrum (a) (% transmission) of the hydrogen bonding base at the desired concentration in carbon tetrachloride was obtained. A second spectrum (b) then was obtained for a solution of the hydrogen bonding acid with the same concentration of the base in carbon tetrachloride, in the same cell and under the same instrumental conditions. The intensities of the two curves then were measured at closely spaced points and the position of the hydrogen bonded band was obtained from a plot of $\log I_a/I_b$ vs. frequency.

Materials.—Reagent grade carbon tetrachloride from freshly opened bottles was used as solvent. Merck reagent grade phenol was purified by fractional crystallization, then vacuum distillation, b.p. 85.5-86.0 (20 mm.). Fractional distillation was employed to purify commercial samples of N,N-dimethylformamide (b.p. 151-153°, n_D^{25} 1.4282; lit. b.p. 153°, n_D^{25} 1.4269¹⁶), N,N-dimethylacetamide (b.p. 162-163°, n_D^{25} 1.4359; lit. b.p. 165°, n_D^{25} 1.4351¹⁶) and 1,2-dimethoxyethane (b.p. 82-83°, n_D^{25} 1.3771; lit. b.p. 84.5-85°, n_D^{25} 1.3798¹⁷).

The straight chain alkynes and diphenylacetylene were obtained from Farchan Research Laboratories, Inc., propargyl halides from K and K Laboratories and phenylacetylene from Eastman Kodak. These commercial

sions about acidities of acetylenes generally confirm those of the Scottish workers.

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(14) After this paper was submitted, a publication by Brand, Eglinton and Morman appeared¹⁵ in which relative acidities of a number of acetylenes were measured by a similar method. Our conclu-

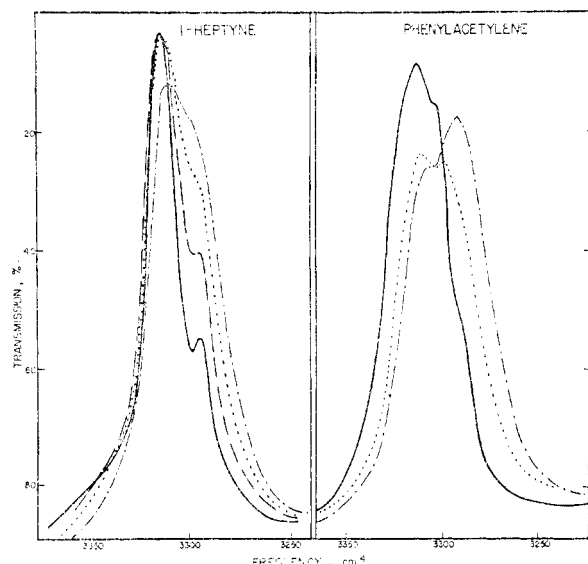


Fig. 1.—C-H stretching absorption bands for acetylenes at various concentrations: for 1-heptyne: —, 0.01 to 0.1 *M*; ---, 1 *M*; ·····, 3 *M*; - - - - , pure liquid. For phenylacetylene: —, 0.006 to 1 *M*; ·····, 4 *M*; - - - - , pure liquid.

acetylenes were purified by drying over phosphorus pentoxide and fractionally distilling; 1-hexyne (b.p. 70–70.5°, n_D^{20} 1.3953; lit. b.p. 72°, n_D^{20} 1.3982¹⁸), 2-hexyne (b.p. 78–80°, n_D^{20} 1.4098; lit. b.p. 86°, n_D^{20} 1.4135¹⁸), 3-hexyne (b.p. 79–80°, n_D^{20} 1.4081; lit. b.p. 81.5–82°, n_D^{20} 1.4108–1.4116¹⁸), 1-heptyne (b.p. 95–97°, n_D^{20} 1.4063; lit. b.p. 100–101°, n_D^{20} 1.4084¹⁸), 1-octyne (b.p. 125–126°; lit. b.p. 126–127°¹⁸), 2-octyne (b.p. 136–139°, lit. 138°¹⁸), 3-octyne (b.p. 131–132°, lit. 134–135°¹⁸), 4-octyne (b.p. 129°; lit. 131.5°¹⁸), phenylacetylene (b.p. 139.5–140°, n_D^{20} 1.5460; lit. b.p. 144–145°, n_D^{20} 1.5489¹⁹), propargyl bromide (b.p. 82.0–82.5°, n_D^{20} 1.4897; lit. b.p. 82°, n_D^{20} 1.4952²⁰), propargyl chloride (b.p. 56.0–56.5°; lit. 56–57°²¹). Diphenylacetylene was recrystallized from 95% ethanol; residual ethanol was removed under vacuum (2 mm.) for 3 hr. at room temperature, m.p. 60–61°; lit. 60–61°.²² Methoxyacetylene was kindly donated by Mr. Edward Conklin, while ethyl propiolate (b.p. 119°; lit. 117°²³) was prepared by esterifying a sample of propiolic acid donated by Mr. Howard Whitlock.

Phenylacetylene-*d*₁.—A Grignard reagent solution was prepared from 33.6 g. (0.27 mole) of *n*-propyl bromide and an equivalent amount of magnesium in 200 ml. of ether, in a 500 ml. flask fitted with a reflux condenser, stirrer and dropping funnel, under a nitrogen atmosphere. A mixture of 18.3 g. (0.20 mole) of phenylacetylene with 20 ml. of dry triethylamine was added to the Grignard solution over 10 minutes with cooling. The propane which was released was condensed in a trap at –70°. The flask was allowed to warm to room temperature and 5.4 g. (0.27 mole) of deuterium oxide was added with stirring, after which the mixture was allowed to stand overnight. Most of the ether was then distilled from the reaction flask. The mixture next was cooled and filtered to remove magnesium salts, the solids were washed well with ether and the filtrate and washings were combined and fractionally distilled. About 9 g. (50%) of crude phenylacetylene-*d*₁ was collected at 130–140°. Redistillation afforded 4.4 g. of pure product, b.p. 139.5–140.5°. Infrared analysis showed that less

than 5% undeuterated phenylacetylene was present in the sample. A similar method was used to prepare 1-hexyne-*d*₁.

1-Phenyl-1-propyne.—The method used was similar to one previously employed for the synthesis of 1-phenyl-1-butyne.²⁴ The sodium derivative of phenylacetylene was prepared from 4.8 g. (0.041 mole) of phenylacetylene and an equivalent amount of sodium in 20 ml. of dry toluene at 35°. The suspension was heated to 70–75°, and 7.6 g. (0.041 mole) of freshly-distilled methyl *p*-toluenesulfonate was added with stirring over thirty minutes. The mixture was stirred at 75–80° for 2 hr. and then cooled. Ether (30 ml.) was added and the liquid was decanted away from the white solid residue, which then was washed with 10 ml. of ether. The decantate and washings were dried and fractionated, yielding 1.9 g. (40%) of colorless liquid product, b.p. 77–79° (18 mm.), n_D^{20} 1.5595; lit. b.p. 71–74° (15 mm.), n_D^{20} 1.561.²⁵ The purity of the product was established by gas chromatography. The compound showed a doublet C≡C stretching band in the infrared spectrum at 2273 and 2235 cm.^{–1}.

Discussion

Acetylenes as Hydrogen Bonding Acids. The Acetylenic C–H Stretching Band.—The C–H stretching absorption band in a terminal acetylene normally falls near 3315 cm.^{–1},²⁶ and the structure is inherently complex. In addition to the principal peak at about 3314 cm.^{–1}, weak side bands near 3300 cm.^{–1} are found which persist in dilute solution (Fig. 1) and in the vapor phase. Nyquist and Potts attribute these side bands to Fermi resonance, but the fact that they are also found in deuterated acetylenes makes this explanation unlikely. The nature of these side bands is now under investigation in our laboratories. For all of the compounds in this study except methoxyacetylene, ν_{C–H} was found between 3306 and 3315 cm.^{–1}. Upon deuteration, the C–D absorption in 1-hexyne and phenylacetylene appears near 2595 cm.^{–1}.²⁷ Methoxyacetylene shows abnormally high C–H and C≡C frequencies of 3328 and 2162 cm.^{–1}, respectively. Unusually high force constants for the C≡C and C–H bonds in methoxyacetylene may result from electron release from oxygen to the triple bond. Perhaps *p* orbitals on oxygen overlap with pi orbitals of the carbon atoms, with consequent electron delocalization and strengthening of the C≡C and C–H bonds.

To study the effect of hydrogen bonding on the acetylenic C–H stretching frequency, the compounds *N,N*-dimethylacetamide (DMA) and *N,N*-dimethylformamide (DMF) were chosen since they are sufficiently basic to influence the C–H stretching band markedly and are preferable to tertiary amines since they have little absorption in the 3000 cm.^{–1} region. Some measurements were made with the less basic material 1,2-dimethoxyethane (GDME) in order to compare our results with those of Murahashi, *et al.*⁸ Our Δν_{CH} values for hydrogen bonding to this base are somewhat smaller than those reported by the Japanese workers, probably because these workers used solutions of acetylenes in pure GDME, while our measurements are for

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acetylenes and GDME both dissolved in carbon tetrachloride solvent.

In monosubstituted acetylenes, electronegative substituents should enhance the acidity of the acetylenic hydrogen and hence increase the enthalpy of hydrogen bonding to a given base. This increase might be reflected in an increased C-H bond shift upon hydrogen bonding to the base.²⁸ The C-H frequency shifts upon hydrogen bonding to a given base do increase when alkyl substituent groups are replaced by electron-attracting groups such as halomethyl and phenyl. Methoxyl also increases the band shift compared to alkyl groups, but the increase is quite small. Since the inductive effect of a methoxyl group is strongly electron-withdrawing ($\sigma_1 = +0.25$),²⁹ the small shift is a further indication of a resonance interaction between oxygen and the triple bond. The most strongly acidic acetylene studied was ethyl propiolate. In this compound both inductive and resonance effects may operate to enhance the acidity.²⁹

Acetylenes as Hydrogen Bonding Bases.—The relative Lewis basicity of acetylenes was determined by measuring the shift of the phenol O-H stretching frequency upon hydrogen bonding to the acetylenes. This technique previously was used to measure the relative basicities of olefins¹³ and has been used widely for other types of compounds in the past.³⁰ The 1-alkynes give $\Delta\nu_{OH} = 90$ cm.⁻¹ with phenol (Table I) compared to 70 cm.⁻¹ for 1-alkenes¹² and 47 cm.⁻¹ for benzene. Acetylenes apparently are somewhat stronger bases toward phenol than are simple terminal olefins or aromatic hydrocarbons. When the terminal hydrogen in the 1-alkynes is replaced by a methyl group, the electron availability at the triple bond is increased, and the $\Delta\nu_{OH}$ increases greatly to about 132 cm.⁻¹. A further small but apparently real increase in $\Delta\nu_{OH}$ to about 137 cm.⁻¹ takes place when the methyl group is replaced by ethyl or *n*-propyl in the 3- and 4-alkynes.

The aryl acetylenes show two bonded OH peaks with phenol. With phenylacetylene the peaks appear at $\Delta\nu_{OH} = 41$ and 80 cm.⁻¹ and can be attributed to hydrogen bonding to the aromatic ring and to the triple bond, respectively. When the terminal hydrogen in phenylacetylene is replaced by a methyl group, the basicity of the triple bond is greatly increased, and the two peaks now appear at 44 and 108 cm.⁻¹. The triple bond in 1-phenyl-1-propyne is slightly more basic than that in 1-alkynes, indicating that phenyl groups may be more electron-donating than hydrogen atoms toward the electronegative (sp hybrid) acetylenic carbon atoms.

Because of the electron-withdrawing effect of the halogen atoms, the propargyl halides should be less basic than 1-alkynes. However, the $\Delta\nu_{OH}$ values of about 40 cm.⁻¹ shown by these compounds seem

too small for hydrogen bonding to the triple bond. The observed shifts are in the right range for hydrogen bonds from phenol to halogen atoms in alkyl halides³¹ and so may represent principally hydrogen bonding to halogen.

TABLE I
FREQUENCY SHIFTS OBSERVED FOR ACETYLENES, $RC\equiv CR'$ ^a

R	R	CH	$\Delta\nu_{CH}$, DMA	$\Delta\nu_{CH}$, DMF	$\Delta\nu_{CH}$, GDME	$\Delta\nu_{OH}$, PhOH
<i>n</i> -C ₄ H ₉	H	3314	74	61	36 ^b	90
<i>n</i> -C ₅ H ₁₁	H	3314	74	61		90
<i>n</i> -C ₆ H ₁₃	H	3314	72	59		90
C ₆ H ₅	H	3314	91	78	62, 72 ^d	41, ^b 80 ^b
BrCH ₂	H	3313	94	82	64	41 ^b
ClCH ₂	H	3314	94	83		32 ^b
CH ₃ O	H	3328	81			
COOC ₂ H ₅	H	3306	123		84, 104 ^d	
CN	H	3304			153 ^d	
<i>n</i> -C ₄ H ₉	D	2599		30 ^b		90
C ₆ H ₅	D	2593	46		36	40, ^b 75 ^b
<i>n</i> -C ₄ H ₉	CH ₃					133
C ₂ H ₅	C ₂ H ₅					138
<i>n</i> -C ₆ H ₁₁	CH ₃					132
<i>n</i> -C ₄ H ₉	C ₂ H ₅					137
C ₃ H ₇	C ₄ H ₇					137
C ₆ H ₅	C ₆ H ₅					42, ^b 80 ^c
C ₆ H ₅	CH ₃					44, ^b 108 ^b

^a The columns headed $\Delta\nu_{CH}$, DMA, $\Delta\nu_{CH}$, DMF, and $\Delta\nu_{CH}$, GDME give the frequency shifts observed for the acetylenic CH (or CD) stretching band upon admixture with *N,N*-dimethylacetamide, *N,N*-dimethylformamide and 1,2-dimethoxyethane, respectively. The column headed $\Delta\nu_{OH}$, PhOH gives the frequency shift for the phenol OH stretching band upon hydrogen bonding to the acetylene. All values ± 2 cm.⁻¹ except: ^b ± 5 cm.⁻¹; ^c ± 10 cm.⁻¹; ^d Data from ref. 8 for alkynes dissolved in pure base.

Intermolecular Association of Terminal Acetylenes.—The fact that terminal acetylenes have both proton-donating and proton-accepting ability suggests that association by intermolecular hydrogen bonding might take place in these compounds, as it does in hydroxyl compounds. Some spectral evidence for such association has been presented previously.^{7,8,10,15} To investigate this possible association more fully, the C-H stretching bands of phenylacetylene, 1-heptyne, 1-hexyne, 1-octyne and propargyl bromide and chloride were studied at several concentrations of the acetylenes in carbon tetrachloride solution and in the pure liquids. The spectral absorption curves for the first two compounds listed are shown in Fig. 1. As the concentration of the acetylenic compound is increased, with corresponding decrease in path length so that very nearly the same number of molecules are under examination in each experiment, a new absorption band appears on the low-frequency side of the C-H fundamental at concentrations above 1 *M* (Fig. 1). The differences in frequency between the new band and the fundamental are small, 12–14 cm.⁻¹ for 1-alkynes, 14–17 cm.⁻¹ for propargyl halides and 22 cm.⁻¹ for phenylacetylene.

This spectral evidence indicates that intermolecular hydrogen bonding takes place in all of the termi-

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nal acetylenes studied.³² However, the small band shifts indicate that the hydrogen bonds are weak. Furthermore, the spectra show that association is quite incomplete even in the pure liquids. The

(32) The hydrogen bonding in the 1-alkynes must take place between the acetylenic hydrogen on one molecule and the π electrons of the triple bond on another. In phenylacetylene and the propargyl halides, the π electrons of the aromatic ring and the unshared electron pairs on the halogens can also serve as basic sites in intermolecular hydrogen bonding.

effect of the intermolecular association upon the gross physical properties of 1-alkynes therefore is slight.

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Mechanism of Influencing the Thermal Decomposition of Propionaldehyde by Nitric Oxide

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The mechanism of influencing the thermal decomposition of propionaldehyde by nitric oxide is established. The correctness of the mechanism as described is partially supported by the fact that the values of the influencing factors found experimentally and calculated on the basis of the mechanism agree excellently in each case. From this mechanism it is evident that the double effect experimentally found can be ascribed to the fact that a portion of the chain carrying radicals is combined with nitric oxide and the ratio of the reactions occurring with stabilized and non-stabilized radicals causes the inhibition or the catalysis, depending on its concentration.

I. Introduction

More than two decades ago Hinshelwood and his co-workers¹ had observed that the rate of the thermal decomposition of organic substances is altered markedly by nitric oxide. The most striking feature was that in certain cases nitric oxide, depending on its concentration, could either increase or decrease the velocity of the *same* process. In order to interpret the inhibiting effect by nitric oxide, it was reasonable to suppose that nitric oxide combines with chain carrying radicals and thus reduces the rate of the process. However, the interpretation of the catalytic effect of nitric oxide has remained essentially unexplained. All the endeavors aiming to establish the mechanism of the reaction affected by nitric oxide, especially in the case of the double effect, have been unsuccessful, owing to the lack of systematic experiments necessary to throw light on this problem.

Some years ago Szabó and his co-workers^{2,3} had published their conception by which the influencing by nitric oxide, even also its double effect can be unitarily interpreted. According to the theorem of stabilization of free radicals, nitric oxide forms a more or less stable complex with the chain carriers. These stabilized and non-stabilized radicals then react either with each other or with the molecule of the initial substance. In other words this means that the stabilization of the radicals results in new rupturing and propagating steps, the rate of which may considerably differ from those of the corresponding reactions of the non-stabilized radicals. Thus the same substance may exert two entirely opposite effects depending only on the ratio of concentrations which determine whether the reaction steps of the original non-

stabilized radicals or those of the stabilized radicals are dominating. Because at that time the lack of data in the literature had rendered it possible to prove this theory only roughly, very detailed and systematic investigations have been performed in order to elucidate the mechanism of the effect of nitric oxide. As is well known, nitric oxide exerts a double effect on the thermal decomposition of propionaldehyde. Therefore this reaction seemed to be a proper model for the above purposes.

II. Experimental Method and Results

The apparatus applied in the experiments has already rendered good services at our institute.⁴ By applying glass valves instead of greased stopcocks and by carefully keeping impurities off the reaction zone, it was possible to work under extremely clean conditions.

From experimental data it became evident that the thermal decomposition of propionaldehyde is not a monomolecular process of first order—as supposed by Hinshelwood and his co-workers^{5,6}—but the reaction runs down according to the Rice-Herzfeld mechanism with rupturing of β, β type.⁷ The reaction of this type has the order $3/2$ which was proved by our experimental data, *i.e.*, from the dependence of the initial rate on the pressure, from the time of the half-change, and by following the course of the experiments in time. To lend support to the above facts, rate constants calculated according to the first and $3/2$ order are compared in Table I. Rate constants calculated according to order $3/2$ are summarized in Table II.

From the dependence of rate constants on temperature 52.4 ± 1 kcal. is obtained for the activation energy of the process. Our calculations on the order of reaction and the activation energy are supported by Boyer and Niclaude's⁸ investigations, too. They found the same order from the dependence of the initial rates on pressure and 50.3 ± 2 kcal. for the activation energy.

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