

# Evidence for Alkali Metal Induced Intermolecular Acetylenic Hydrogen Atom Transfer between Hydrogen-Bonded Alkyne Complexes in Solid Argon

Laurent Manceron and Lester Andrews\*

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901 (Received: July 24, 1984; In Final Form: April 8, 1985)

Condensation of acetylene, propyne, and 2-butyne/acetylene mixtures with heavy alkali metal atoms (Na, K, Cs) in an argon matrix at 15 K has led to the appearance of infrared absorptions due to ethylene, propylene, and *trans*-2-butene, respectively. These results stand in sharp contrast with the products obtained with lithium. Isotopic studies have shown that ethylene formation involved three different acetylene molecules and evidenced a difference in the product yield with hydrogen vs. deuterium as well as a preference for *trans*- vs. *cis*-C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> formation, which is discussed and rationalized by differences in the zero point energies for the different mixed deuterium isotopes of the intermediate vinyl radical. This trend is amplified by methyl substitution. Spectroscopic evidence was found in these experiments for cesium acetylide (Cs<sup>+</sup>C<sub>2</sub>H<sup>-</sup>) and a cesium-acetylene  $\pi$  complex, which are involved in the intermolecular acetylenic hydrogen atom transfer process.

## Introduction

In recent years, the important use of organoalkali compounds as catalysts for polymerization of olefins, as well as their increasing use as reagents in organic synthesis or intermediates for the preparation of various kinds of organometallic compounds,<sup>1</sup> has stimulated a great deal of theoretical and experimental research. At the macroscopic scale, direct action of alkali metals on unsaturated hydrocarbons has been used for addition to carbon-carbon double bonds,<sup>2</sup> for metal/hydrogen exchange if the corresponding carbanion has evidenced some stability,<sup>3</sup> for metal/halogen exchange in all cases, and finally for a hydrogenation agent using liquid ammonia as reaction medium and hydrogen source.<sup>4</sup>

Metal atom cryochemistry, where metal atoms are condensed with reactants in a large argon excess to isolate the reaction intermediate, has been widely used to study complexation of various  $\pi$  systems (acetylene, ethylene, propylene, benzene) by transition-metal atoms.<sup>5</sup> Interaction of alkali metals with acetylene at a microscopic scale, without solvent effects or influence of the reaction medium, presents an interesting problem as it could proceed through weak complexation or radical formation as an alternative to the rather unfavorable charge transfer (EA = -1.8 eV).<sup>6</sup> A matrix ESR study has reported reactions of Na atoms with acetylene, and characterized charge-transfer species, the most stable one identified as vinylidene radical anion, and has observed the vinyl radical in concentrated samples of acetylene.<sup>7</sup> In a previous paper, we have described the results of a study of the lithium and acetylene matrix system, which gave LiC<sub>2</sub>H<sub>2</sub> and Li<sub>2</sub>C<sub>2</sub>H<sub>2</sub> molecules where lithium symmetrically bridges the  $\pi$  system, perturbs the C<sub>2</sub>H<sub>2</sub> group, and bends it away from linearity.<sup>8</sup> We present here an infrared study of the reaction products obtained by codeposition of heavy alkali metal (Na, K, or Cs) with acetylene, propyne, and 2-butyne molecules diluted in solid argon.

## Experimental Section

The cryogenic refrigeration system, vacuum vessel, alkali metal source, and experimental techniques have been described earlier.<sup>9</sup>

(1) "Handbook of Organometallic Compounds", N. Hagihara, M. Kumada, and R. Okawara, Ed., W. A. Benjamin, New York, 1968.

(2) (a) J. A. Morrison, C. Chung, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 5015 (1975); (b) L. A. Shimp, C. Chung, and R. J. Lagow, *Inorg. Chim. Acta*, **29**, 77 (1978).

(3) R. Nast and J. Gremm, *Z. Anorg. Allg. Chem.*, **325**, 62 (1963).

(4) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33**, 337 (1937).

(5) (a) H. Huber, G. A. Ozin, and W. J. Power, *J. Am. Chem. Soc.*, **98**, 6509 (1976); (b) G. A. Ozin, D. McIntosh, W. J. Power, and R. P. Messmer, *Inorg. Chem.*, **20**, 1782 (1981); (c) P. Kasai, *J. Am. Chem. Soc.*, **105**, 6704 (1983); (d) J. H. B. Chenier, J. A. Howard, B. Mile, and R. Sutcliffe, *J. Am. Chem. Soc.*, **105**, 788 (1983); (e) J. A. Howard, R. Sutcliffe, J. S. Tse, and B. Mile, *Organometallics*, **3**, 859 (1984).

(6) S. Y. Chu, L. Goodman, and R. Okawana, *J. Am. Chem. Soc.*, **97**, 7 (1975).

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(8) L. Manceron and L. Andrews, *J. Am. Chem. Soc.*, **107**, 563 (1985).

Sodium and potassium metal (Baker and Adamson, 99.9%) were vaporized directly from the liquid phase, whereas an atomic beam of cesium was generated by reaction of molten lithium metal (Fisher) and cesium chloride (Fisher) in a Knudsen cell maintained at 300 °C.<sup>10</sup> High-purity acetylene (Matheson) and argon (Air Products, 99.995%), <sup>13</sup>C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>D<sub>2</sub> (MSD Isotopes) were used without further purification. 2-Butyne (provided by R. N. Grimes) and propyne (Matheson) were frozen, thawed, and outgassed at liquid nitrogen temperature before use.

In each experiment, 40 mmol of gaseous argon and the reactant mixture were injected in about 18 h. The mixture was condensed on a cold CsI window (~15 K) simultaneously with the metallic vapor effusing from the Knudsen cell. In order to estimate the yield of product in the experiment, the total amount of matrix trapped on the deposition window (0.75 ± 0.05 mmol) was derived from the interference fringe patterns recorded on the spectrum after deposition. This value was checked by measuring band areas of the two IR-active bands of the precursor ( $\nu_3$  and  $\nu_3$ ) in blank experiments and deriving the amount of acetylene trapped from the integrated absorptions measured by previous workers.<sup>11</sup> Assuming an equal trapping rate for argon and acetylene, one obtains 0.7 ± 0.1 mmol of matrix deposited, in agreement with the previous result. Similar measurements were also carried out with blank samples of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub>. Infrared spectra were recorded with a Beckman IR-12 and a Perker-Elmer 983 spectrometer with data station. The spectra presented here were processed against a background collected with the bare CsI window and then base-line corrected to compensate for matrix scattering. Frequency accuracy is better than ±0.5 cm<sup>-1</sup> with slidewidths of 1 cm<sup>-1</sup> in the product band regions.

## Results

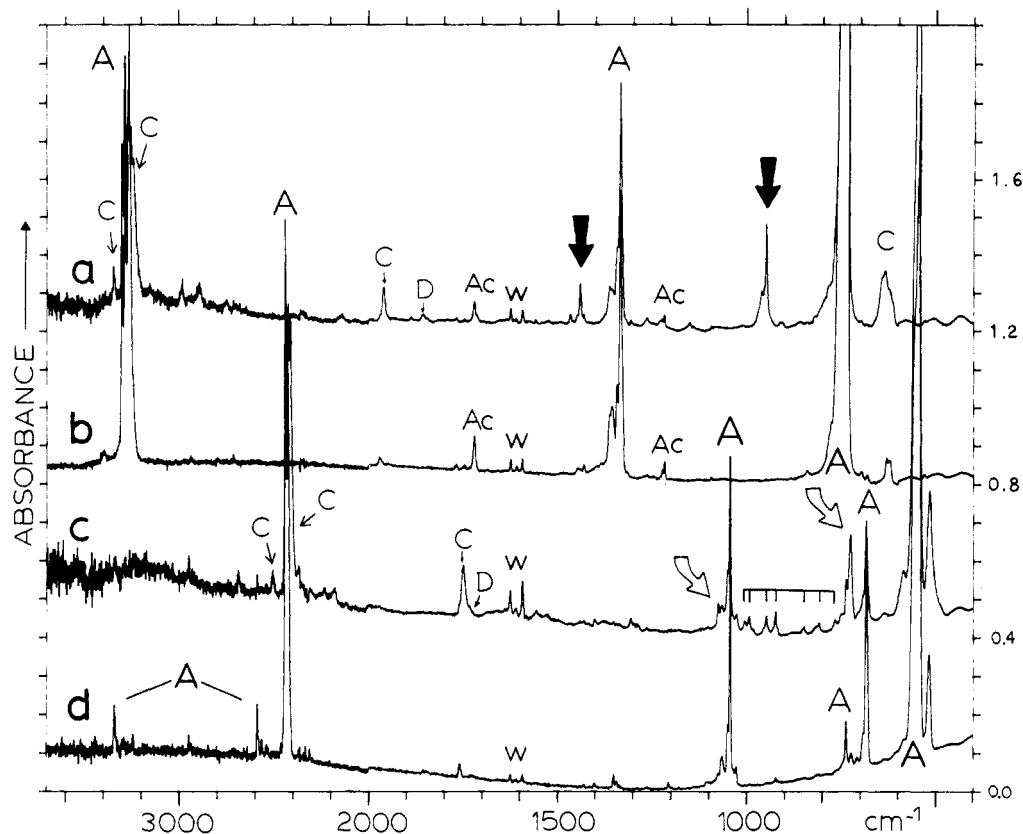
Alkali metal matrix reactions will be described for three alkyne systems.

**Acetylene and Alkali Metals.** Several experiments were run depositing sodium, potassium, and cesium atoms with different acetylene/argon mixtures in order to determine the best reaction conditions. In all the experiments there arose only two sets of new absorptions. The first set (marked C in Figure 1) is characterized by broad absorptions slightly shifted from the position of the different fundamentals of acetylene, whereas the other set (marked by arrows) shows sharp lines completely separated from parent molecule absorptions. Although no frequency shift was detected (within measurement accuracy) for these new product bands with the different alkali metals, a 2-3-fold increase in product yield was observed when going from sodium to cesium

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(10) L. Andrews, J.-T. Hwang, and C. Trindle, *J. Phys. Chem.*, **77**, 1065 (1973).

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**Figure 1.** Infrared spectra recorded after condensation of  $0.75 \pm 0.05$  mmol of argon/acetylene = 200/1 mixture at 15 K for 18 h: (a)  $C_2H_2$  + cesium atoms; (b)  $C_2H_2$  without cesium atoms; (c)  $C_2D_2$  with cesium atoms; (d)  $C_2D_2$  without cesium atoms. A designates acetylene fundamentals or combination bands of the different isotopic species of acetylene; W and Ac designate water and acetone absorptions present as impurities. The bold arrows indicate  $C_2H_4$  product bands, and open arrows denote absorptions due to  $C_2D_4$  product.

**TABLE I: Gas-Phase and Matrix Fundamentals ( $\nu$ ,  $cm^{-1}$ ) for Ethylene and Deuterium-Substituted Isotopes**

$C_2H_4$				$C_2H_3D$		$t-C_2H_2D_2$			$c-C_2H_2D_2$			$C_2HD_3$		$C_2D_4$				
gas <sup>a</sup>		matrix <sup>b</sup>		gas <sup>c</sup>	matrix <sup>b</sup>	gas <sup>c</sup>		matrix <sup>b,d</sup>	gas <sup>c</sup>		matrix <sup>b</sup>	gas <sup>c</sup>	matrix <sup>b</sup>	gas <sup>a</sup>		matrix <sup>b</sup>		
$\nu$	A	$\nu$	A	$\nu$	$\nu$	$\nu$	A	$\nu$	$\nu$	$\nu$	$\nu$	$\nu$	$\nu$	$\nu$	A	$\nu$	A	
$\nu_4$				1000	1003	988	37.0	992				764	765					
$\nu_7$	949.2	81.8	947	115	809	807	727	24.8	725	843	71.9	847	723		720	41.8	722	88
$\nu_8$					943							918	922					
$\nu_{12}$	1443.5	9.8	1440	19.5	1404	1399	1300	7.7	1298	1344	6.9	1335	1290	1305	1078	5.2	1073	10.8

<sup>a</sup>R. Golike, I. Mills, W. Person, and B. L. Crawford, Jr., *J. Chem. Phys.*, **25**, 1267 (1956); A ( $km\ mol^{-1}$ ) is the extinction coefficient. <sup>b</sup>This work. <sup>c</sup>Reference 14. <sup>d</sup>Reference 13.

for similar experimental conditions.

Figure 1 presents spectra recorded for reaction of Cs atoms with normal and deuterated acetylene, contrasted with blank sample spectra. With normal acetylene the most prominent product is characterized by two bands at 1440 and  $947.2\ cm^{-1}$  (with a broad shoulder at  $960\ cm^{-1}$ ). These bands shift to  $1074$  and  $724\ cm^{-1}$  with the deuterated precursor and other weak signals given in Table I appear, whose relative intensities vary with the amount of  $C_2H_2$  and  $C_2HD$  traces in the experiments. The observation of the mixed H/D counterparts of the product at  $1440$  and  $947\ cm^{-1}$  requires careful comparison with blank spectra, for two of these bands overlap some of the parent molecule ( $\nu_4 + \nu_5$  combination of  $C_2D_2$  and  $\nu_5$  of  $C_2H_2$  present in traces in the  $C_2D_2$  sample). Figure 2 illustrates the relative intensity changes in the  $1399$ -,  $1305$ -,  $1295$ -,  $1003$ -,  $991$ -,  $922$ -,  $847$ -, and  $764\ cm^{-1}$  bands with different  $C_2H_2/C_2D_2$  ratios. These changes allow separation of the latter bands into several groups, which will be assigned to  $C_2H_xD_y$  species ( $x + y = 4$ ), as given in Table I.

Irradiation has been carried out with medium- and high-pressure mercury arcs without any noticeable change in the entire spectrum; likewise annealing does not further affect the sharp bands but increases the broad  $960\ cm^{-1}$  band.

Careful comparison with blank experiments run without metal also evidences weak new features at  $3345$ ,  $3240$ ,  $1960$ , and  $632$

$cm^{-1}$  (labeled C in Figure 1) as listed in Table II. The two signals at  $1960$  and  $632\ cm^{-1}$  overlap weakly activated  $\nu_2$  and  $\nu_4$  acetylene fundamentals in the dimer and polymers at  $1971$  and  $621\ cm^{-1}$ ,<sup>5b,10</sup> but are one order of magnitude more intense. The signal at about  $3240\ cm^{-1}$  forms a shoulder on the low-frequency side of the  $3265\ cm^{-1}$   $\nu_3$  band of the hydrogen-bonded  $C_2H_2$  dimer reported by previous workers.<sup>12</sup> Finally, other weak absorptions ( $A = \text{absorbance} = 0.02$ ) at  $1856$  (labeled D),  $2978$ ,  $2890$ , and  $1265\ cm^{-1}$  are seen in the most concentrated cesium experiments, and these bands grow on annealing the matrix.

**Propyne and Cesium.** When cesium atoms were codeposited with propyne, extra absorptions at  $1649$ ,  $1452$ ,  $997$ ,  $909.5$ , and  $582\ cm^{-1}$  were produced, along with a weak feature at  $2124\ cm^{-1}$  shouldering the  $2135\ cm^{-1}$   $\nu(C\equiv C)$  mode of propyne.

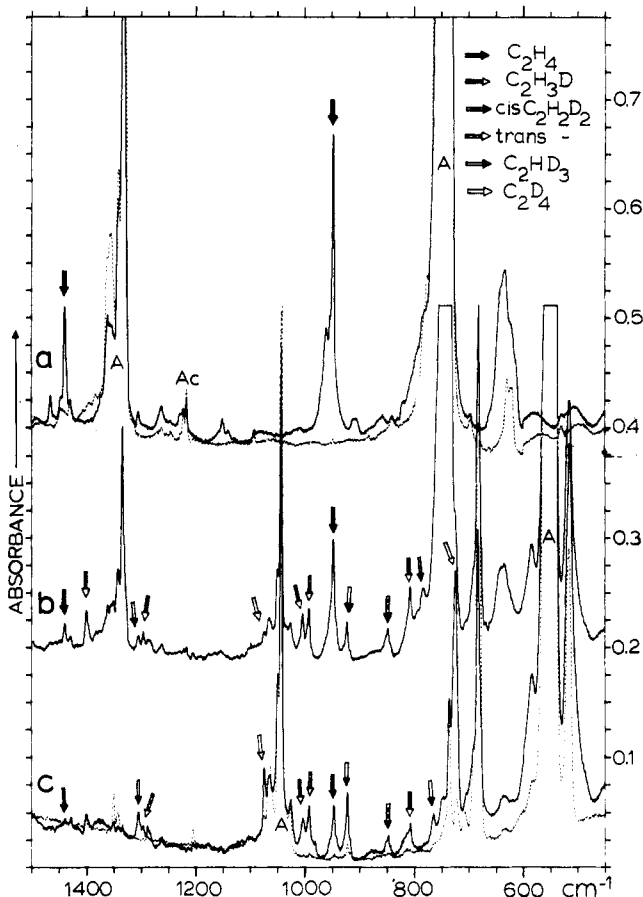
**2-Butyne and Acetylene and Cesium.** Figure 3 shows the result of addition of cesium atoms to an acetylene/2-butyne (DMA) mixture. In addition to the C features and the  $947\ cm^{-1}$  absorption already observed in experiments with acetylene as the only hydrocarbon reagent, a sharp absorption was observed at  $976.2\ cm^{-1}$ , which shifted to  $755\ cm^{-1}$  when deuterated acetylene was used. A broad, weak feature also appeared at  $1890\ cm^{-1}$  between the

(12) N. Baganskis and M. Bulanin, *Opt. Spectrosc.*, **29**, 687 (1970); **35**, 525 (1972).

**TABLE II: New Absorptions ( $\text{cm}^{-1}$ ) Produced by Codeposition of Alkali Metal Atoms (Na, K, Cs) and Acetylene in Solid Argon, Compared to Fundamentals of Acetylene in the Gas Phase**

mode	$\text{C}_2\text{H}_2^a$	$\text{M} + \text{C}_2\text{H}_2$	$\text{C}_2\text{D}_2^a$	$\text{M} + \text{C}_2\text{D}_2$	product label
$\Sigma_g(\nu_1)\nu_1\text{CH}$	3374	3345	2701	2680	C
$\Sigma_u(\nu_3)\nu_3\text{CH}$	3295 (3300) <sup>b</sup> 3283 (3285) <sup>b</sup>	$\sim 3240$	2439 (2442) <sup>b</sup>	$\sim 2410$	C
$\Sigma_g(\nu_2)\nu_{cc}$	1974 (P, 1971) <sup>d</sup>	1960 <sup>c</sup> 1856	1762 (P, 1760)	1749 1735	C D
$\Pi_u(\nu_5)\delta_s\text{CCH}$	730 (737) <sup>b</sup>		537 (544) <sup>b</sup>		
$\Pi_g(\nu_4)\delta_s\text{CCH}$	612 (P, 620)	632	505 (P, 512)	515	C

<sup>a</sup>Gas-phase data, ref 17. <sup>b</sup>Matrix data; this work. <sup>c</sup>The  $^{13}\text{C}_2\text{H}_2$  counterpart was  $1898\text{ cm}^{-1}$ . <sup>d</sup>P = polymers.



**Figure 2.** Expanded scale infrared spectra of the CCH bending region for different argon/acetylene ( $\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2$ ) = 200/1 mixtures with and without cesium atoms in an argon matrix: (a)  $\text{C}_2\text{H}_2/\text{C}_2\text{HD}/\text{C}_2\text{D}_2 = 1/0/0$ , solid line is with Cs atoms, dotted line is without Cs atoms; (b)  $\text{C}_2\text{H}_2/\text{C}_2\text{HD}/\text{C}_2\text{D}_2 = 0.33/0.04/0.63$  with Cs atoms; (c)  $\text{C}_2\text{H}_2/\text{C}_2\text{HD}/\text{C}_2\text{D}_2 = 0.005/0.055/0.94$ , solid line is with Cs atoms, dotted line is without Cs atoms. A designates acetylene fundamentals or combination bands of the different isotopic species, and Ac designates acetone impurity absorptions.

C and D species absorptions, but it does not shift upon deuteration. None of these features was observed in a cesium experiment with 2-butyne and no acetylene.

### Discussion

The new products of the matrix reaction of alkynes with heavy alkali metal atoms will be identified and reactions occurring in the matrix will be considered.

**Identification.** The complexity of the pattern observed in isotopic mixtures shows unambiguously that the main reaction product contains more than two hydrogen atoms; moreover, the coincidence of the position and relative intensity of the two product bands with the two strongest  $\nu_7$  and  $\nu_{12}$  bands of ethylene observed at  $947$  and  $1440\text{ cm}^{-1}$  ( $I_{947}/I_{1440} \approx 5$ ) with  $\text{C}_2\text{H}_4$  and  $722$  and  $1073\text{ cm}^{-1}$  ( $I_{722}/I_{1073} \approx 9$ ) with  $\text{C}_2\text{D}_4$  in solid argon is striking. In the isotopic mixture experiments, the signals observed at  $764.5$ ,  $922$ , and  $1305\text{ cm}^{-1}$  match exactly the strongest  $\text{C}_2\text{HD}_3$  absorptions

(observed as an impurity in a  $\text{C}_2\text{D}_4$  blank sample), whereas the bands at  $847\text{ cm}^{-1}$ , on the one hand, and  $991$  and  $1298\text{ cm}^{-1}$ , on the other hand, correspond to the positions of the strongest absorptions of *cis*- and *trans*- $\text{C}_2\text{H}_2\text{D}_2$  in an argon matrix.<sup>13</sup> The other reported strong absorptions at  $725$  and  $1335\text{ cm}^{-1}$  would be overlapped by  $\nu_5$  and  $\nu_4 + \nu_5$  of  $\text{C}_2\text{H}_2$ . The remaining species absorbs at  $1399$ ,  $1003$ , and  $807\text{ cm}^{-1}$ , close enough to the positions of  $\nu_{12}$ ,  $\nu_4$ , and  $\nu_7$  of  $\text{C}_2\text{H}_3\text{D}$  (reported at  $1404$ ,  $1000$ , and  $809\text{ cm}^{-1}$  in the gas phase)<sup>14</sup> to confirm the identification of  $\text{C}_2\text{H}_3\text{D}$ . Therefore all the different mixed H, D isotopes of ethylene (except  $\text{CH}_2\text{CD}_2$ ) were observed as reaction products of  $\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2$  in presence of alkali atoms.

A fact immediately obvious from the appearance of  $\text{C}_2\text{HD}_3$  and  $\text{C}_2\text{H}_3\text{D}$  reaction products in the  $\text{C}_2\text{D}_2$  sample (96%  $\text{C}_2\text{D}_2$ , 4%  $\text{C}_2\text{HD}$ ) is that the process must involve three different acetylene molecules, since  $\text{C}_2\text{HD}$  is only present as an impurity. It is possible to estimate the amount of ethylene formed in the different experiments by band area measurement and comparison with integrated absorption gas-phase data, or matrix isolated  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$ . In two successive experiments run with  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$  in similar experimental conditions,  $0.95 \pm 0.1\text{ }\mu\text{mol}$  of  $\text{C}_2\text{H}_4$  was formed in the first case while the amount of  $\text{C}_2\text{D}_4$  detected in the second case was  $0.7 \pm 0.1\text{ }\mu\text{mol}$ . Two observations are also very striking when comparing the distribution of the different deuterium isotopes. For instance, in the experiment presented in Figure 2c, only traces of  $\text{C}_2\text{H}_2$  and a small amount of  $\text{C}_2\text{HD}$  (4%) were present: (i) A noticeable decrease in product yield with deuteration occurred:  $8 \times 10^{-2}\text{ }\mu\text{mol}$  of  $\text{C}_2\text{H}_4$  and  $17.4 \times 10^{-2}\text{ }\mu\text{mol}$  of respectively *trans*- and *cis*- $\text{C}_2\text{H}_2\text{D}_2$  were formed, compared with the  $\text{C}_2\text{D}_4$  amount cited above. These data give a  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_2\text{D}_2/\text{C}_2\text{D}_4 = 1/2.8/8.8$  ratio instead of the  $1/650/49000$  ratio obtained from a purely statistical model with identical H/D reaction rates. The lack of knowledge of the  $\text{C}_2\text{H}_3\text{D}$  and  $\text{C}_2\text{D}_3\text{H}$  extinction coefficient does not allow further quantitative comparison of the  $\text{C}_2\text{D}_2$  vs. the  $\text{C}_2\text{H}_2$  reaction rate, but relative band intensities support this trend. (ii) There exists roughly a 3.4/1 ratio for the *trans*- and *cis*- $\text{C}_2\text{H}_2\text{D}_2$  product formed, which indicates that, in the process of addition of a first hydrogen atom to a  $\text{C}_2\text{D}_2$  or  $\text{C}_2\text{H}_2$  precursor, the *trans* intermediate is favored.

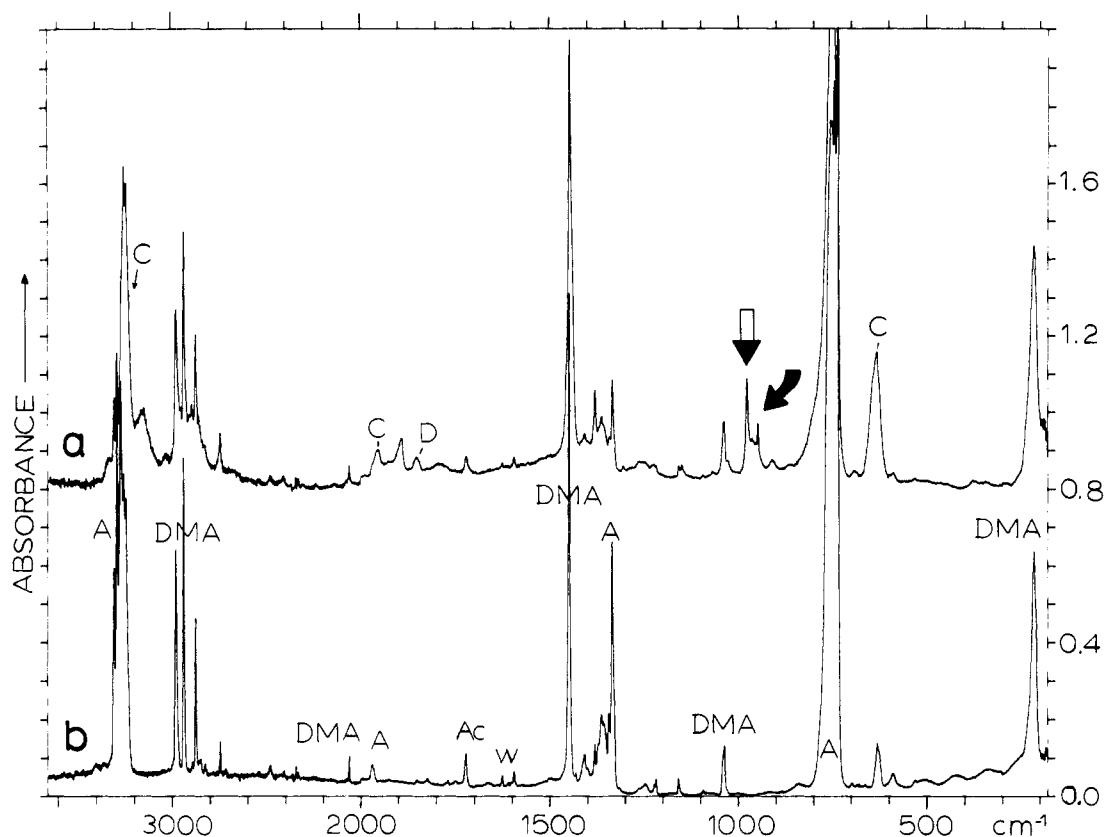
The product observed with propyne can be identified by following the above alkali metal induced alkyne hydrogen transfer to the alkyne triple bond: the five observed product bands match (within  $1\text{ cm}^{-1}$ ) the five strongest absorptions of propylene.<sup>15</sup> The main product observed with 2-butyne is formed in presence of acetylene and is characterized by one sharp absorption at  $976.2\text{ cm}^{-1}$  ( $755\text{ cm}^{-1}$  with  $\text{C}_2\text{D}_2$ , H/D ratio 1.293), which is coincident with the strongest line of *trans*-2-butene (H-C=C-H out-of-plane deformation)<sup>15</sup> whose other strong absorption (methyl group deformation) would not be shifted enough from parent butyne bands to be observed here. Fortunately, however, the spectrum shows unambiguously that no band is present at  $680\text{--}685\text{ cm}^{-1}$  where *cis*-2-butene, the other possible isomer, would have its strongest absorption,<sup>16</sup> thereby indicating that methyl group

(13) M. E. Jacox, personal communication.

(14) B. L. Crawford, Jr., J. E. Lancaster, and R. G. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953).

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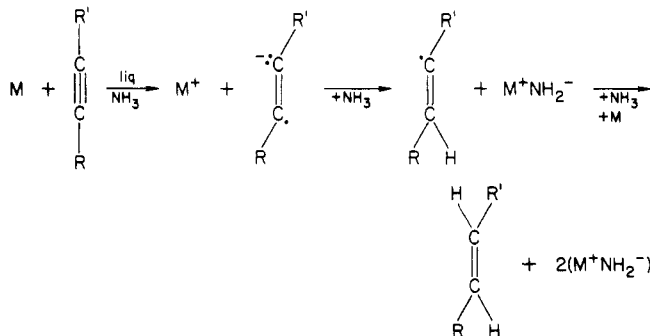
**Figure 3.** Infrared spectra recorded after deposition of 0.75 mmol of argon/2-butyne (DMA)/acetylene = 200/0.5/1 mixture at 15 K for 18 h: (a) with cesium atoms; (b) without cesium atoms. A designates acetylene fundamentals or combination bands and DMA the fundamentals of 2-butyne, W and Ac water and acetone impurity absorptions. The bold arrow indicates the  $C_2H_4$  product band already observed with acetylene as the only reagent, and the black-headed arrow denotes the new product observed with the addition of 2-butyne.

substitution of acetylenic hydrogen favors even more a trans hydrogenation.

The broad bands labeled C in Figure 1 are only slightly shifted from acetylene absorptions with no noticeable difference for Na, K, and Cs, and no new features were observed for  $C_2H_2/C_2D_2$  mixtures. The C bands are present in dilute acetylene experiments and are thus likely to belong to a species containing one acetylene molecule. An important fact is that the absorption observed at  $1960\text{ cm}^{-1}$  shifts upon deuteration to  $1749\text{ cm}^{-1}$ , the same amount as acetylene ( $\nu(C\equiv C)$ ,  $1974$  to  $1762\text{ cm}^{-1}$  in the gas phase);<sup>17</sup> therefore, this species contains two hydrogen atoms, the  $200\text{-cm}^{-1}$  deuterium shift indicating a similar  $\nu(C\equiv C)/\nu_{\text{sym}}(C-H)$  coupling as in acetylene itself. (In the ethynyl radical ( $HC_2$ ) only a  $100\text{-cm}^{-1}$  shift was observed for the  $C\equiv C$  stretching mode on deuteration.)<sup>18</sup> For these reasons, the C bands are assigned to a weak alkali metal/acetylene van der Waals  $\pi$  complex of  $C_{2v}$  symmetry with the  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$  modes activated,<sup>17</sup> although we cannot completely exclude the possibility that alkali metal atoms could induce enough asymmetry in the argon lattice to create such a perturbation of  $C_2H_2$  molecules.

The band labeled D at  $1856\text{ cm}^{-1}$  with  $C_2H_2$  is produced on reagent codeposition and it grows markedly upon annealing along with the broad  $960\text{-cm}^{-1}$  absorption. The latter band is due to a more perturbed ethylene formed in acetylene aggregates by cesium atom diffusion. In the deuterated acetylene experiments, the only counterpart which could be found for the  $1856\text{-cm}^{-1}$  band is the broad  $1735\text{-cm}^{-1}$  shoulder on the C complex absorption. The relative magnitude of the deuterium shift as well as a comparison with previous data obtained for alkali metal acetylide salts ( $1825\text{--}1860\text{ cm}^{-1}$ )<sup>3</sup> suggests assignment of this signal to the  $C\equiv C$  stretching mode of the acetylide anion in the  $Cs^+C_2H^-$  ion pair; however, the failure to observe the methyl-substituted counterpart with propyne precludes a definite assignment, although the

#### SCHEME I



mechanism to be described below requires the  $Cs^+C_2H^-$  species. The band observed at  $1890\text{ cm}^{-1}$  with 2-butyne, cesium, and acetylene does not show any acetylene deuterium shift and cannot be assigned in this work.

**Reactions Occurring in the Matrix.** Alkali metal induced hydrogenation of alkynes has been observed in liquid ammonia<sup>4</sup> where the proposed mechanism first involved metal atom valence electron transfer and then proton transfer from ammonia in two steps (Scheme I). The trans addition is favored because the intermediate radical anion is supposed to prefer a trans configuration.

In an ESR matrix isolation study of the  $Na/C_2H_2$  interaction, Kasai reported evidence for three charge-transfer species differing by their photoactivation energies.<sup>7</sup> None of them can be identified here, although multiple irradiations were performed. Interaction between metal and the very weakly perturbed acetylene group of complex C seems very unlikely to involve charge transfer. However, at higher acetylene concentration, Kasai observed the vinyl radical, the intermediate in the formation of ethylene, the latter of which was produced in this work. Kasai suggested that hydrogen bonding plays a key role in the process of hydrogenation for vinyl radical formation, which has already been proposed from

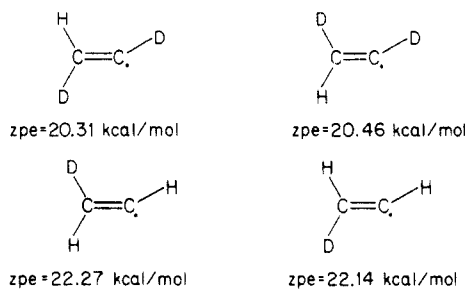
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gas-phase kinetic data where a 3/1 HCl/propylene ratio was found necessary for hydrogen chloride addition to propylene.<sup>19</sup> This proposal is also supported by the fact that heavy alkali metal codeposited with ethylene in similar infrared experiments gives no evidence for reaction product;<sup>20</sup> it is well-known that acetylenic C-H bonds exhibit acidic character and therefore undergo stable hydrogen bonding<sup>12,21,22</sup> as opposed to weak van der Waals interaction loosely bonding the ethylene dimer.<sup>23,24</sup> Therefore, vinyl radicals are generated by addition of one alkali metal atom to an acetylene dimer, as suggested by Kasai,<sup>7</sup> then further encounter with another metal-acetylene van der Waals pair will lead to formation of ethylene and a second metal acetylide (Scheme II). The latter is probably species D absorbing at 1856 cm<sup>-1</sup> (1735 with C<sub>2</sub>D<sub>2</sub>), which is obviously a much weaker infrared absorber. The sharpness of the ethylene product bands, the lack of frequency shift when going from Na to Cs, and agreement with matrix-isolated ethylene<sup>15</sup> might indicate that this product is formed at the liquid-solid interface during the growth of the matrix sample and then surrounded by argon atoms, while the 960-cm<sup>-1</sup> broad absorption might correspond to more perturbed ethylene formed by reaction of two metal atoms and the acetylene trimer in the matrix.

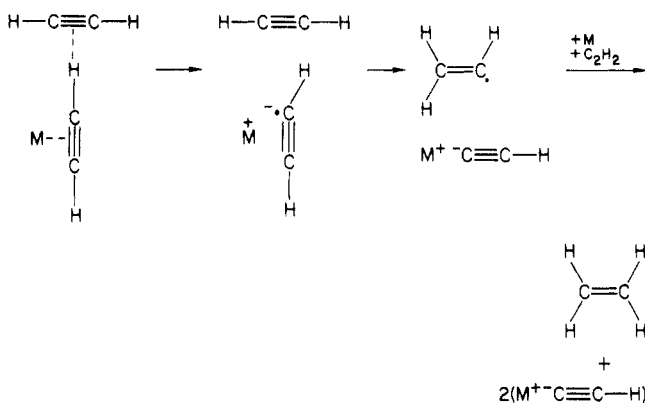
Similar lithium-acetylene experiments gave a bridged LiC<sub>2</sub>H<sub>2</sub> species and no evidence for ethylene.<sup>8</sup> The higher ionization energy of lithium and its ability to form a strong  $\pi$  complex make formation of the charge-transfer intermediate leading to the acetylide more difficult, and the latter species is required for intermolecular H-atom transfer.

It is also interesting to consider the preference experimentally shown for *trans*-dideuterioethylene and *trans*-2-butene. In a complete theoretical investigation of the H + C<sub>2</sub>H<sub>2</sub> → C<sub>2</sub>H<sub>3</sub> reaction, Harding et al. have computed an equilibrium geometry for the vinyl radical, and harmonic frequencies and zero point energies for the different deuterium isotopes.<sup>25</sup> If we compare their results for the four different mixed hydrogen-deuterium isomers



one sees that the zero point energies favor the *trans* form by 0.15 kcal/mol ( $\sim 52$  cm<sup>-1</sup>) for addition of H atoms to a C<sub>2</sub>D<sub>2</sub> precursor,

#### SCHEME II



but the *cis* form by 0.13 kcal/mol ( $\sim 45$  cm<sup>-1</sup>) for addition of D atoms to a C<sub>2</sub>H<sub>2</sub> precursor. Assuming a 50 K temperature (above which proper isolation is no longer experimentally possible with argon) one obtains an overall 2.8/1 *trans/cis* Boltzmann population ratio close to the 3.4/1 experimentally observed. Of course a kinetic isotope effect, impossible to estimate from the data but a plausible explanation for the C<sub>2</sub>D<sub>4</sub>/C<sub>2</sub>H<sub>4</sub> yield discrepancy, would lower the temperature required to obtain the observed *trans/cis* ratio. Furthermore, the 8 kcal/mol inversion barrier<sup>26</sup> for the vinyl radical would, of course, forbid *cis-trans* interconversion at these temperatures. Substitution of hydrogens by two methyl groups seems to favor even more in *trans* hydrogen addition product.

#### Conclusions

Codeposition of heavy alkali metal atoms (Na, K, and Cs) with acetylene and methyl-substituted acetylenes in an argon matrix gives evidence for alkali metal induced intermolecular acetylenic hydrogen transfer to the C≡C triple bond to form ethylene. Spectroscopic evidence was obtained for a weak cesium-atom-acetylene  $\pi$  complex and cesium acetylide, which are involved in the intermolecular hydrogen atom transfer mechanism. These results are substantially different from the product of similar lithium studies and provide support for the role of hydrogen-bonded intermediates prior to hydrogen atom transfer. The addition also shows a preference for hydrogen relative to deuterium transfer, and a *trans* isomer selectivity (partial with C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> and total with C<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>), which is tentatively rationalized in terms of differences in zero point energies for the vinyl radical intermediate structures.

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**Registry No.** Na, 7440-23-5; K, 7440-09-7; Cs, 7440-46-2; D<sub>2</sub>, 7782-39-0; C<sub>2</sub>H<sub>4</sub>, 74-85-1; C<sub>2</sub>H<sub>3</sub>D, 2680-00-4; *t*-C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>, 1517-53-9; *c*-C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>, 2813-62-9; C<sub>2</sub>HD<sub>3</sub>, 2680-01-5; C<sub>2</sub>D<sub>4</sub>, 683-73-8; acetylene, 74-86-2; propyne, 74-99-7; 2-butyne, 503-17-3; cesium acetylide, 30180-52-0.

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