Structure of the Bromovinyl Radical: a Matrix Isolation Study

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The bromovinyl radical has been prepared by the reaction of bromine atoms with acetylene in an argon matrix at 17 K and its i.r. spectrum has been studied. The spectrum of $C_2HDBr^{\bullet}$ shows the presence of two isomers, indicating that the radical has an unsymmetric structure.

The structure of the vinyl radical seems to be well established; theoretical calculations [1,2] point to a structure which resembles an ethylene molecule, with one hydrogen atom removed and where the HCC angle of the lone hydrogen atom is increased to *ca.* 131—135°.[1,2] The e.s.r. spectrum of the vinyl radical has been studied by several groups,[3-5] and their results are consistent with the theoretically calculated structure. The fluorovinyl radical ($CHFCH^{\bullet}$) has been studied both by e.s.r.[6,7] and by i.r. spectroscopy;[8] the results indicate that this radical has a structure similar to that of the vinyl radical, and the e.s.r. data are interpreted as support for a structure with the fluorine atom *cis* to the lone hydrogen atom.

The stereochemistry of the free-radical additions of hydrogen bromide and bromine to olefins and acetylene has been studied by many investigators.[9] The initial step in these reactions is the addition of a bromine atom to the unsaturated CC bond. Whether this intermediate has a cyclic structure, with the bromine atom bound equally to both carbon atoms, or a classical structure like that of the vinyl radical has been discussed extensively.[10] The e.s.r. investigation of Abell and Piette[11] gives evidence for the existence of a bridged symmetrical structure, but the assignment of the spectrum has been questioned by Symons.[12] For the $(CH_3)\dot{C}C(Br)(CH_3)_2$ radical, Maj *et al.* conclude from e.s.r. data that it is unsymmetrical at 77 K, and that bromine exchange between the two equivalent sites becomes fast on the e.s.r. time scale at 100 K.[13]

This paper is a continuation of a series of i.r. and u.v. absorption spectroscopic studies of complexes between halogen atoms and small molecules by the matrix-isolation technique.[14-16] When bromine atoms were added to acetylene, we obtained a product with an i.r. spectrum entirely different from that of the acetylene atomic iodine complex. As will be discussed, we assign the i.r. spectrum to the bromovinyl radical.

Experimental

Argon–bromine mixtures prepared by standard manometric techniques were passed through a 20 cm long quartz oven kept at about 1 250 K, and then immediately condensed on the cold CsI window of a cryostat. Acetylene–argon mixtures were simultaneously condensed on the cryostat window without passing through the oven. The cryostat window was kept at 17 K with an Air Products CS208 refrigeration system. The deposition rate was about 9 mmol h^{-1}. Bromine atom production was checked as described in ref. 14.

Acetylene was distilled and degassed on a vacuum line. The i.r. spectrum showed no impurity lines. [$^2H_2$]Acetylene was prepared from CaC_2 and D_2O (Norsk Hydro 99% D) degassed and distilled. [$^2H_1$]Acetylene was prepared from CaC_2 and a mixture of equal volumes of H_2O and D_2O, distilled and degassed. The resulting gas was an equilibrium mixture of C_2H_2, C_2D_2 and C_2HD. Bromine was distilled and degassed. Argon (L'Air Liquide 99.9995%) was passed through a glass spiral in liquid oxygen before use.

I.r. spectra were run on a Bruker 113v FTIR spectrometer at 0.5 cm^{-1} resolution.

Assignment

The spectrum of acetylene in solid argon has been studied by Bagdanskis *et al.*[17] Our spectra agreed with theirs.

When molecular bromine and acetylene were codeposited in an argon matrix, a set of new bands appeared. Their positions were all very close to those of acetylene complexed with atomic and molecular iodine, and they are assigned accordingly. In addition to the fundamentals of complexed acetylene, we also observed the Br_2 stretching fundamental of complexed Br_2, activated by the complex formation. Table 1 summarizes the assignments for the acetylene–molecular bromine complex.

When bromine atoms were introduced into an acetylene-containing matrix, a set of new bands appeared. In contrast to the $C_2H_2{\cdot}Br_2$ bands, their positions were not close to the acetylene fundamentals. The bromine atoms were always accompanied by varing amounts of water, hydrogen bromide, carbon monoxide, and carbon dioxide, and we have observed bands due to the acetylene–hydrogen bromide complex,[18] the acetylene–water complex,[19] and the water–hydrogen bromide

Table 1. Observed fundamentals (cm^{-1}) of the acetylene complexes with Br_2 and I_2 (Ar; 17 K)

	Br_2	C_2H_2	$C_2H_2{\cdot}Br_2$	$C_2H_2{\cdot}I_2$	C_2D_2	$C_2D_2{\cdot}Br_2$	$C_2D_2{\cdot}I_2$	C_2HD	$C_2HD{\cdot}Br_2$	$C_2HD{\cdot}I_2$
ν_1								3 340.9	3 331.9	3 330.7
ν_2		1 973.8[a]	1 969.4	1 968.8	1 762.4[a]	1 760.9	1 760.3	1 856.7	1 849.6	1 850.3
ν_3		3 302.5								
					2 441.8	2 435.3	2 434.7	2 586.4	2 579.5	2 578.7
		3 288.6	3 281.7	3 280.4						
ν_4								519.1	524.2	523.7
ν_5		736.7	741.2	743.5	542.7	546.1	547.2	683.3	688.6	690.4
				741.7						689.0
ν_{Br_2}	[316[b]]			310		310			310	

[a] Ref. 17. [b] Ref.29.

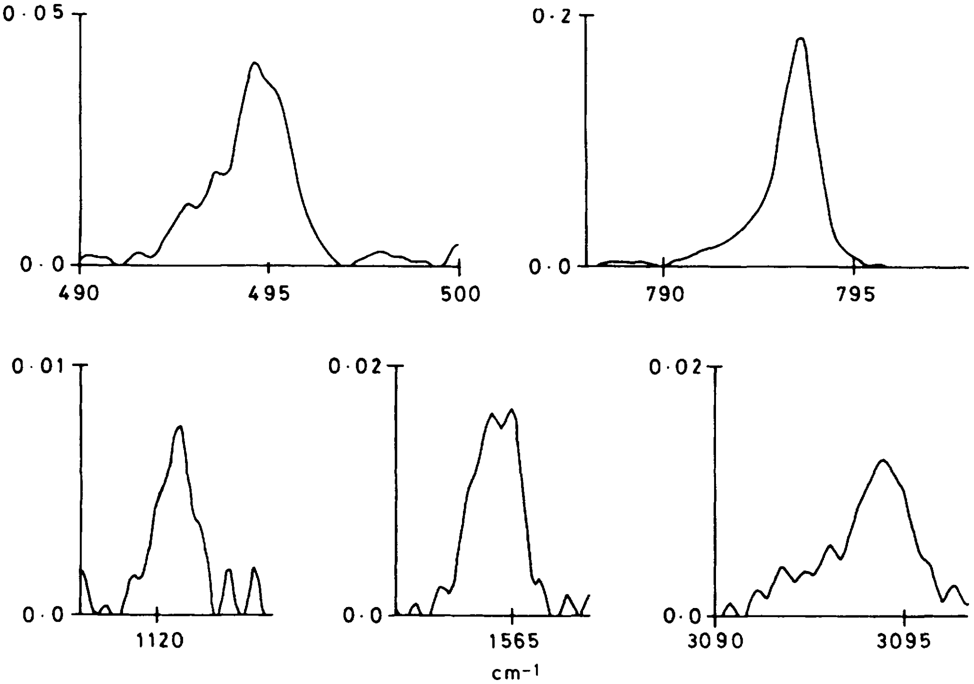

Figure 1. Observed absorption bands of $C_2H_2Br^{\bullet}$ (Ar; 17 K); Ar:C_2H_2 155:1; Ar:Br_2 72:1; 22 mmol of Ar deposited

Table 2. I.r. spectrum of the vinyl bromide radical (cm^{-1}; 17 K; Ar matrix)

$C_2H_2Br^{\bullet}$		$C_2D_2Br^{\bullet}$		$C_2HDBr^{\bullet}$	
Peak position	Relative intensity	Peak position	Relative intensity	Peak position	Relative intensity
494.6	2.7	479.7	0.5	485.1	0.8
793.6	8.2	572.9	1.0	577.2	1.6
		600.5	0.6		
1 120.4	0.4	827.8	0.2		
1 564.4	1	1 506.4	1	1 531.0	1
				1 549.4	0.4
3 093.8	0.7	2 288.5	0.08	2 402.5	0.5

complex.[20] The effects of bromine atoms on Br_2, CO, CO_2, HBr, and H_2O were checked in separate experiments. After depositions at high concentrations of Br_2 (1:50) and acetylene (1:100), weak bands due to *cis*- and *trans*-1,2-dibromoethylene were observed. Experiments where the matrix was irradiated during the deposition of C_2H_2–Br_2–Ar and C_2D_2–Br_2–Ar mixtures produced these compounds in relatively large concentrations. Their band positions were all close to those reported for the gaseous and liquid dibromoethylenes.[21,22] In addition to the bands which we could assign to various impurities as already described, a set of five new bands was observed with C_2H_2 and Br. Their relative intensities were constant in all experiments, and the intensity of the strongest band varied between 0.36 and 0.03. They are assigned to $C_2H_2Br^{\bullet}$ (see Figure 1 and Table 2). With C_2D_2 instead of C_2H_2, we observed six bands, with constant relative intensities, which could not be assigned to impurities and which we therefore assign to $C_2D_2Br^{\bullet}$ (Figure 2 and Table 2). When an equilibrium mixture of C_2H_2, C_2D_2, and C_2HD was allowed to interact with $Br^{\bullet}$, we observed, in addition to the $C_2H_2Br^{\bullet}$ and $C_2D_2Br^{\bullet}$ spectra, five new bands. Their relative intensities were constant and the maximum intensity of the strongest band varied between 0.09 and 0.012; they are therefore assigned to $C_2HDBr^{\bullet}$ (Table 2).

We have not observed any band which we could assign to a weak complex between atomic bromine and acetylene, similar to the complex between atomic iodine and acetylene.[16]

Discussion

When bromine atoms are codeposited with acetylene in an argon matrix, they react to from bromovinyl radicals; iodine atoms and acetylene under the same conditions only form a weak atom–molecule complex.[16] This difference is not surprising; from heats of formation data[23] one may estimate the enthalpy of addition of a bromine atom or an iodine atom to acetylene as -7 and 7 kcal mol^{-1}, respectively. From activation energy data[24,25] one can estimate an activation energy of 1.3 kcal mol^{-1} for the addition of a bromine atom to acetylene. This seems high in view of the low matrix temperature, but since the deposition time is 2—4 h, a measurable fraction of the bromine atoms trapped together with an acetylene molecule may react, even if the activation energy is high. For an activation energy of 1 kcal mol^{-1}, the reaction would be expected to be complete.

Unfortunately, we have not been able to observe all fundamentals of the bromovinyl radical, and we are therefore unable to make a detailed assignment of its i.r. spectrum. However, comparisons with the data of Jacox[8] on the fluorovinyl radical and of Elst *et al.*[26] on vinyl bromide (Table 3) make it clear that the 1 564.4 cm^{-1} band of $C_2H_2Br^{\bullet}$ and the 1 506.4 cm^{-1} band of $C_2D_2Br^{\bullet}$ are due to the C=C stretching fundamental. For $C_2HDBr^{\bullet}$ there are two C=C bands, at 1 531.0 and 1 549.4 cm^{-1}, but there is only a single band each for $C_2H_2Br^{\bullet}$ and $C_2D_2Br^{\bullet}$ (Figure 3). For a bridged non-classical bromovinyl radical, only a single $C_2HDBr^{\bullet}$ isomer is expected, whereas for the classical unsymmetrical structure, the two isomers C(Br)H–$\dot{C}$D and $\dot{C}$H–C(Br)D are expected. The bridged symmetric structure is therefore not in accord with the

Table 3. Comparison of the i.r. spectra of vinyl fluoride, [^{2}H]vinyl bromide,[25] the fluorovinyl radical,[8] and the bromovinyl radical (cm^{-1})

	CHF=CDH	$C_2H_2F^•$	$C_2H_2Br^•$	CHBr=CHD	$C_2D_2F^•$	$C_2D_2Br^•$	CDBr=CHD
a′	3 095		3 093.8	3 089			3 052
	3 095			3 057		2 288.5	2 283
	2 265			2 289			2 244
	1 630	1 623	1 564.4	1 575	1 564	1 506.4	1 549
	1 318	1 211	1 120.4	1 297			1 249
	1 235	678		1 244		827.8	1 017
	779			886			805
(c x)[a]	1 137	1 066	494.6	578	1 070	479.7	585
	434	462		336			317
a″	926	785	793.6	940			856
	815	631		793	624	600.5	691
	576			485	485	572.9	532

[a] C-halogen stretching fundamental.

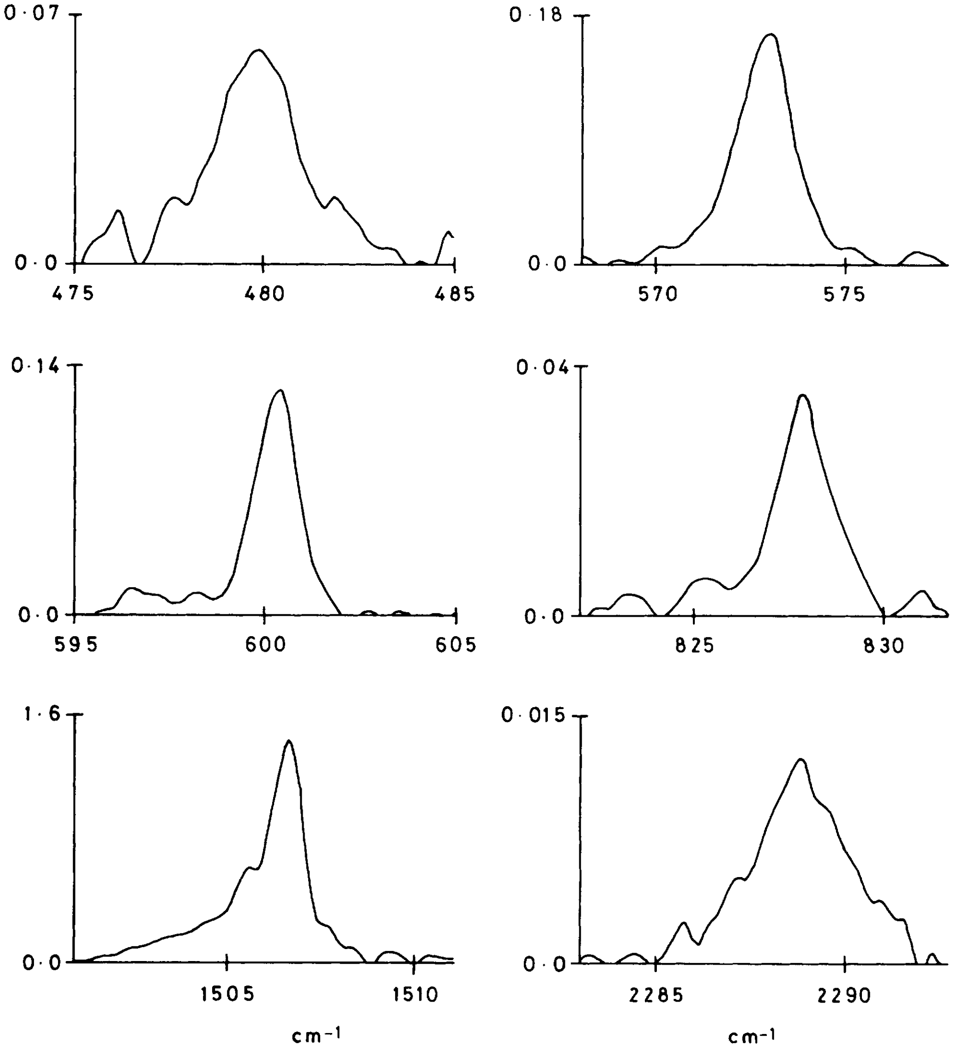

Figure 2. Observed absorption bands of $C_2D_2Br^•$ (Ar; 17 K); Ar:C_2D_2 139:1; Ar:Br_2 53:1; 32 mmol of Ar deposited

experimental result: the bromine atom has to be closer to one of the carbon atoms than to the other.

Let us assume that the bromovinyl radical has a classical vinyl radical structure,[1,2] planar, with a =CHBr group similar to that of vinyl bromide and with a $C{=}\dot{C}{-}H$ angle around 130°, *cis* to the bromine atom. A comparison between the spectra of the bromovinyl radical, the fluorovinyl radical, vinyl bromide, and vinyl fluoride (Table 3) shows that this is not an unreasonable assumption. The observed CH and CD stretching bands of $C_2H_2Br^•$ and $C_2D_2Br^•$ may well be due to the =C(Br)–H and

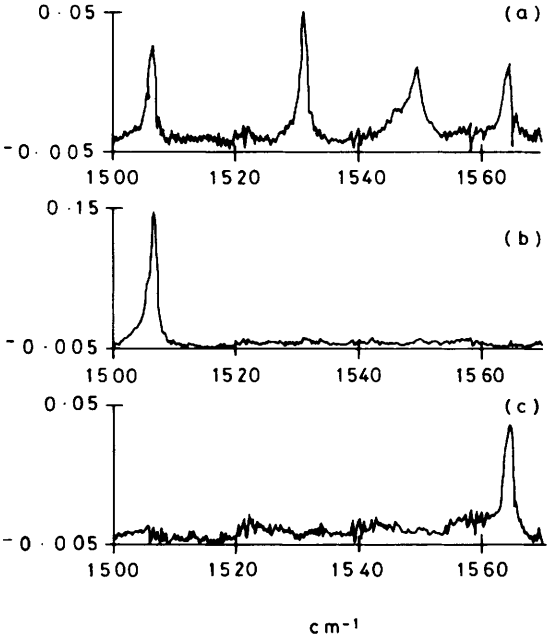

Figure 3. The C=C stretching band (Ar; 17 K); (a) equilibrium mixture of C_2HD, C_2H_2, and C_2D_2; Ar:total acetylene 123:1; Ar:Br_2 56:1; 34 mmol of Ar deposited; (b) Ar:C_2D_2 139:1; Ar:Br_2 53:1; 32 mmol of Ar deposited; (c) Ar:C_2H_2 134:1; Ar:Br_2 54:1; 31 mmol of Ar deposited

=C(Br)–D stretches, respectively. If they are, the 2 402.5 cm^{-1} band of $C_2HDBr^{\bullet}$ must be due to =$\dot{C}$–D of CHBr=$\dot{C}$–D. The corresponding bands of $C_2H_2Br^{\bullet}$ and $C_2D_2Br^{\bullet}$ are then expected in regions where ν_3 bands of $(C_2H_2)_n$, $(C_2D_2)_n$, and HBr complexes make observation of weak bands difficult. The 1 120.4 (827.8) and 793.6 cm^{-1} (600.5) bands seem to be reasonable candidates for the in-plane and out-of-plane hydrogen-bending fundamentals of the =CHBr (=CDBr) groups. The insensitivity of the 494.6 cm^{-1} band to isotopic composition of the radical makes it reasonable to assign it to the C–Br stretching vibration. It is significantly below the C–Br vibration of vinyl bromide (Table 3); *cf.* formaldehyde, where the CH stretches are significantly below those of CH_2=CD_2. McKean[27] has suggested that the *p* lone pair on carbonyl oxygen gives an antibonding contribution to the C–H bonds, bands for which are therefore shifted to lower wavenumbers. This idea is supported by the observation that the formaldehyde CH stretches are shifted towards higher wavenumbers when the carbonyl oxygen lone pair is engaged in complex formation.[28] The unpaired electron of the bromovinyl radical may give a similar antibonding contribution to the CBr bond. Note that the C–F stretch of the fluorovinyl radical is also below that of vinyl fluoride (Table 3).

In conclusion, the i.r. data obtained in this work show that the bromovinyl radical is unsymmetrical, and are consistent with a classical vinyl radical structure.

Acknowledgements

This work was supported by the Swedish Natural Science Research Council and Knut and Alice Wallenberg's Stiftelse.

References

1 W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 1971, **93**, 808.
2 S. Nagase and C. W. Kern, *J. Am. Chem. Soc.*, 1979, **101**, 2544.
3 R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.
4 E. J. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1964, **40**, 213.
5 P. H. Kasai, *J. Am. Chem. Soc.*, 1972, **94**, 5950.
6 E. J. Cochran, F. J. Adrian, and V. A. Bowers, *J. Phys. Chem.*, 1970, **74**, 2083.
7 P. Raghunathan and S. K. Sur, *J. Phys. Chem.*, 1983, **87**, 3383.
8 M. E. Jacox, *Chem. Phys.*, 1980, **53**, 307.
9 J. K. Kochi, 'Free Radicals,' vol. II, Wiley, New York, 1973.
10 P. S. Skell and K. J. Shea in ref. 9.
11 P. I. Abell and L. H. Piette, *J. Am. Chem. Soc.*, 1962, **84**, 916.
12 M. C. R. Symons, *J. Phys. Chem.*, 1963, **67**, 1566.
13 S. P. Maj, M. C. R. Symons, and P. M. R. Trousson, *J. Chem. Soc., Chem. Commun.*, 1984, 561.
14 A. Engdahl and B. Nelander, *J. Chem. Phys.*, 1982, **77**, 1649.
15 A. Engdahl and B. Nelander, *J. Chem. Phys.*, 1983, **78**, 6563.
16 A. Engdahl and B. Nelander, *Chem. Phys. Lett.*, 1984, **106**, 527.
17 N. I. Bagdanskis, M. O. Bulanin, and Yu. V. Fedeev, *Opt. Spectrosk.*, 1970, **29**, 687.
18 L. Andrews, G. L. Johnson, and B. J. Keisall, *J. Phys. Chem.*, 1982, **86**, 3374.
19 A. Engdahl and B. Nelander, *Chem. Phys. Lett.*, 1983, **100**, 129.
20 A. Schriver, B. Silvi, D. Maillard, and J. P. Perchard, *J. Phys. Chem.*, 1977, **81**, 2095.
21 J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, 1955, **33**, 1171.
22 J. M. Dowling, P. G. Puranik, A. G. Meister, and S. I. Miller, *J. Chem. Phys.*, 1957, **26**, 233.
23 S. W. Benson, 'Thermochemical Kinetics,' 2nd edn., Wiley, New York, 1976.
24 P. I. Abell, *Trans. Faraday Soc.*, 1964, **60**, 214.
25 J. M. Tedder and J. C. Walton, *Adv. Phys. Org. Chem.*, 1978, **16**, 51.
26 R. Elst, W. Rogge, and A. Oskam, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 427.
27 D. C. McKean, *Spectrochim. Acta, Part A*, 1975, **31**, 1167.
28 B. Nelander, *J. Mol. Struct.*, 1980, **69**, 59.
29 B. S. Ault, W. F. Howard, Jr., and L. Andrews, *J. Mol. Spectrosc.*, 1975, **55**, 217.

Received 4*th February* 1985; *Paper* 5/191