INFRARED SPECTROSCOPIC INVESTIGATION OF PROPARGYL RADICALS

STABILIZED IN LOW-TEMPERATURE ARGON MATRIX

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In the last 30 years, major attention has been focused on studies of the structure and properties of one of the simplest conjugated systems, the propargyl radical (PR) [1-8]. Direct observation of the C_3H_3 radical and determination of its ionization potential were accomplished for the first time in 1955 in a mass-spectrometric study of the products obtained in the pyrolysis of propargyl iodide (I) [1]. Later, the PR was characterized by EPR spectrum [2] and electronic absorption spectrum [3]. It was shown in [4] that, of the two most probable structures, the C_3H_3 radical must have the structure of the PR radical (II)



This conclusion has been supported by a determination of the "resonance stabilization energy" [5], which is quite large (8.7-9.6 kcal/mole), and also by <u>ab initio</u> quantum-chemical calculations [6, 7], which suggest a planar linear model for the PR. Finally, one more piece of evidence in favor of the structure (II) has been obtained by IR spectroscopic registration of PR frozen in inert gas matrices [8], even though it was identified on the basis of only 3 out of 12 of its absorption bands.

In spite of the fact that the PR structure corresponds qualitatively to an acetylenelike molecule, the simultaneous presence of a free electron and π -orbitals in this radical should lead to a redistribution of electron density, thus affecting the character of the bonds. In turn, this should be reflected in the vibrational spectrum. In the present work, therefore, we have undertaken an IR spectroscopic analysis in more detail than in [8] and a determination of the spin field of the PR, which we obtained by thermal decomposition of (I) and dipropargyl oxalate (IV) and stabilized in an argon matrix at 12 K.

EXPERIMENTAL

The pyrolysis of compounds (I) and (IV) was performed at 900-1050°C and 10^{-2} - 10^{-4} torr in flow-through quartz reactors, 120×5 and 50×5 mm, connected to an optical helium cryostat. Compound (IV) (mp 98-99°C) was prevaporized at 80-85°C. The thermal decomposition products, together with excess argon, were frozen on a CsI substrate chilled to 12 K by a CSW-208 cryogenic system with a closed loop (Air Products and Chemicals). The IR spectra were recorded by means of a Hitachi-Perkin-Elmer 225 spectrophotometer in the 450-4000 cm⁻¹ range.

The vibrational spectra were calculated by means of a set of programs given in [9], for a planar model of the PR with $R_{C^1-C^2} = 1.401$ Å, $R_{C^2-C^3} = 1.213$ Å, $r_{C^1-H^1} = 1.080$ Å, $r_{C^3-H^3} = 1.066$ Å, and $\angle H^1C^1H^2 = 121^\circ$ [6]. The initial values of the force constants were taken from the molecules of methylacetylene (MA) [10, p. 285] and the ethyl radical (ER) [11].

RESULTS AND DISCUSSION

In the IR spectra of the products from the pyrolysis (950-1050°C, $10^{-4}-10^{-5}$ torr) of compound (I) (Fig. 1b, Table 1) and compound (IV) (Table 1) frozen in an argon matrix at 12 K, we observed — in addition to the absorption bands of the original molecules and those of *Deceased

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(1)	Products from pyrol- ysis of (I), 975°C	Assignment	(I V)	Products from pyrol- ysis of (IV), 1000°C	Assignment
3321 s	3321 s 3307 s 3287 w 3249 w 3111 w	$CH = CCH_{2}I + +CH_{3}C = CH$ $C_{3}H_{3}$ $C_{2}H_{2}$ $a)$ $C_{2}H_{2}$	3321 s	3320 s 3307 s 3287 m 3111 w	$(IV) + +CH_3C = CH C_3H_3 C_2H_2 C_3H_3$
3054 w	3097w 3044w	Benzene		3097 w 3043 w	Benzene
	3026w 2340	C ₃ H ₃ CO ₂	2951w	3026 w 2340 vs	C ₃ H ₃ CO ₂
	2156W	a)		2270sh	C ₃ O ₂ ¹³ CO ₂
2140 vw	2138 w 2080 w 1954 w	CO C_3H_3 $CH_2=C=CH_2$	2140 w	2138 vs 2123 s 2097 s 2080 w 1952 w	$COCO^{13}COC_3H_3CH_2=C=CH_2$
1950w	1950 w 1933 w 1810	$CH \equiv CCH_2I$ a) Fulvene		1932 w	a)
	1482 m 1440 w	Benzene C₃H₃	1777 m 1781 m 1787 m 1761 vs	1777 w 1781 w 1787 w 1761 m 1725 m 1705 m 1600 m 1481 m 1439 m	$\left.\begin{array}{c} b\\ b\\ b\\ C_3O_2\\ Benzene\\ C_3H_3+C_2H_4 \end{array}\right.$
1418 m	1418 m 1369 m 1342 w	CH=CCH2I C3H3 Fulvene	1365 w 1301 s 1295 s 1270 m	1368 m 1301 m 1295 m 1270 w	$\left \begin{array}{c} C_{3}H_{3} \\ \end{array} \right \left(IV \right)$
1264 m	1264 m		1181 vs	1181 s	
1176s	1176 m	CH=CCH ₂ I	1175 vs 1164 vs	1175 s 1164 s	(IV)
1157	1157 m		1154 vs 1150 vs	1154 s 1150 s	
1072m	1072 w 1062 m 1040 w	C ₃ H ₃ Benzene	1029 w	1061 m 1039 w	C3H3 Benzene
	1017m 970m	C ₂ H ₃ a)		1016m 968w	C3H3 a)
960 w			960 m 930 w	960 w 945 m	IV C ₂ H ₄
	925 w	Fulvene	910 w		
	900 w	Fulvene?		900 m	
851 s	851 s 837 w	$\begin{vmatrix} CH = CCH_2 I \\ CH_2 = C = CH_2 \end{vmatrix}$		848 m 837 w	$\begin{vmatrix} \mathbf{b} \\ \mathbf{CH}_2 = \mathbf{C} = \mathbf{CH}_2 \end{vmatrix}$

TABLE 1. Vibrational Frequencies (in cm⁻¹) of CH=CCH₂I and (CH=CCH₂OOC)₂ and Products of Their Pyrolysis, in Argon Matrix at 12 K

(1)	Products from pyrol- ysis of (I), 975°C	Assignment	(IV)	Products from pyrol- ysis of(IV), 1000°C	Assignment
.800 s	800 m 770 w 735 w 706 w 686 vs	$CH = CCH_2I$ Fulvene C_2H_2 a) C_2H_2	770 w	770 w 736 s 702 m 685 vs	$(IV)C_2H_2a)C_3H_3$
	675 s 661 s 655 w	Benzene CO ₂ b)	676 s	675 s 661 vs 642 m	(IV) + benzene CO_2 b)
840 vs 637 vs	640 s 637 s	CH=CCH ₂ I			
	629 m 618 s	CH ₃ C=CH C ₃ H ₃	634 s 631 s	634 s 629 s 618 s	(IV) C₃H₃
815 s 568 m	615 sh 568 m 532 m	$CH = CCH_2I$ C_3H_3		532 m	$C_3H_3+C_3O_2$
	482 s	C ₃ H ₃	1	482 s	C ₃ H ₃

TABLE 1 (continued)

a)Bands pertaining to unidentified, unstable molecules. b)Unidentified, stable molecules.

benzene 3097, 3044, 1482, 1040, and 675 cm⁻¹ [12], fulvene 1810, 1342, 925, and 770 cm⁻¹ [12], and methylacetylene (MA) (629 cm⁻¹) - other intense bands at 3307, 686, and 482 cm⁻¹, which in [8] were assigned to the PR. When the matrix was allowed to warm up completely and the pyrolysis products were again isolated in solid argon, these bands disappeared, being replaced in the spectrum (on the background of bands of stable compounds) by bands that newly appeared or became stronger, at 3321, 1253, 642, and 629 cm⁻¹, which are the most intense bands in the IR spectrum of 1,5-hexadiyne (V), the product of PR recombination (Fig. 2a). The formation of (V) is further confirmed by chromatographic/mass-spectrometric analysis of the final products from the pyrolysis of (I), collected when the matrix was warmed up, bands at 3311, 3026, 2080, 1440, 1369, 1062, 1017, 618, and 532 cm⁻¹; in different experiments, the intensities of these bands varied in proportion to the intensities of the radical.

It should be noted that bands at 3249, 2156, 1933, 969, and 706 cm⁻¹ were present in the IR spectrum of the products from the pyrolysis of (I); these bands pertain to unidentified, unstable particles or molecules, since they also disappeared when the matrix was warmed up. However, when the conditions of thermal decomposition were varied, the intensities of these bands were not proportional to the intensities of the bands known to pertain to the PR; and in the IR spectrum of the pyrolysis products from the oxalate (IV), some of these bands were totally absent.

When the pressure in the heating zone was increased to 10^{-2} torr, the content of PR among the reaction products was lowered, while benzene, fulvene, MA, and allene remained as the main components, the formation of which can be explained by secondary reactions of the PR. For example, MA is formed by abstraction of a proton from the organic substrate by the PR, and the MA is partially isomerized to allene; the formation of benzene and fulvene may be related to thermal isomerization of the PR dimer, the diyne (V) [13]. We found supporting evidence for this last conclusion in a special experiment on pyrolysis of (V) with subsequent freezing of the products in an argon matrix. And in fact we found that (V) does not decompose to form PR (in contrast to 1,5-hexadiene, which dissociates under these conditions into allyl radicals AR [14]), instead (V) isomerizes almost completely to benzene and fulvene (Fig. 2b). We did not detect the third product from the isomerization of (V), 3,4-dimethylenecyclobutene (VI), probably because of the excessively high reaction temperature, at which (VI) is unstable and also isomerizes to benzene [13].

Thus, as a result of high-vacuum pyrolysis $(10^{-4}-10^{-5} \text{ torr})$ of the two predecessor compounds (I) and (IV), we have obtained PR and stabilized it in inert matrices; the PR has been identified in the present work on the basis of 12 IR bands. When the pressure in the pyrolysis zone is increased, secondary reactions of the PR result in the formation of MA, allene, benzene, and fulvene:

					·CH2CH		4.11	1	e S
Vibra	Sym-	Approximate type	v, c	m-1		v, 1 1	Gam2U	G3HD2	៤រូបរូ
No.	metry	of vibrations	ex- peri- ment	cal- cula- tion	form of vibration (and potential energy distribution, %)	cal- cal- cula- tion*	ر ک	- ¹ , calculat	ion
1	A1	vСН	3307	3307	qCH (96)	3665	2558(2545) **	3307	2559(2548) **
6	B2	vasCH2	3111	3111	<i>q</i> ^{-CH₂} (100)	3451	3111	2330	2329
63	٩ı	v.CH2	3026	3026	q ⁺ CH ₂ (98)	3345	3026	2220	2213
ຕ	٩ı	vC≡C	2080	2080	QC≔C (85), QC−C (19)	2342	1959	2063	1947
4	A,	6CH2 2×686	1440 1369	1443	αCH_2 (45), βCH_2 (38), $Q C = C$ (12)	1606	1438	1215 ***	1204 ***
10	\mathbf{B}_2	6rCH2	1062	1061	βCH_2 (90), γCCC (9)	1160	1061	878	876
S	A1	vC-C	1017	1016	$QC-C$ (70), αCH_2 (10), $QC=C$ (8) βCH_2 (8)	1072	1002	851 ***	*** \$}8
11	B2	\$CH	686	684	βCH (85), γCCC (21)	875	611	662	573
9	B,	рСН	618	618	ρCH (86), ρCCC (29)	852	566 (568) **	618	558(553) **
7	Bı	ρ _w CH ₂	532	530	ρCH ₂ (83), ρCCC (15)	568	504	480	428
12	B2	\$CCC	482	484	YCCC (70), BCH (16)	406	407	444	385
8	B	pCCC	!	423	ρCCC (60), ρCH ₂ (16), ρCH (9)	443	365	359	334
	_	_	_	-	-	-	_	-	

TABLE 2. Interpretation of Vibrational Spectrum of Propargyl Free Radical

*Frequency values were taken from [7] with an error up to 10%. **Numbers given in parentheses represent experimental frequencies from [8]. *** $\alpha(CD_2)$ is mixed with QC-C.



Fig. 1. IR spectra (Ar matrix, 12 K): a) C_3H_3I ; b) products from pyrolysis of C_3H_3I (975°C, 10⁻⁵ torr). The arrows indicate absorption bands of the C_3H_3 radical (B = benzene, F = fulvene, U = bands pertaining to unidentified, unstable molecules).



From the experimentally determined IR spectrum of the PR, we were able to carry out a well-founded theoretical calculation that was of assistance in refining the assignment of the observed absorption bands to normal vibrations and in determining the force field of this radical (Tables 2 and 3).

According to quantum-chemical calculations reported in [6, 7], PR is a planar acetylenelike molecule with C_{2V} symmetry, and it should have 12 normal vibrations that are active in the IR spectrum $(5A_1 + 3B_1 + 4B_2)$. In analyzing the spectrum that is obtained for the PR, it is convenient to examine separately the vibrations of the ethynyl and methylene groups, since these vibrations are quite characteristic for each group.

Ethynyl Group. In the PR, this group has four vibrations $(2A_1 + B_1 + B_2)$, all of their bands being registered in our IR spectrum. Thus, the strong band at 3307 cm⁻¹ (in [8] at 3310 or 3305 cm⁻¹) has been assigned to the stretching vibration of the C-H bond (vCH); this value is slightly lower than the analogous band frequencies for stable compounds with the ethynyl group, for example vCH for MA 3322 cm⁻¹, for (V) 3321 cm⁻¹, and for propargyl halides 3320-3325 cm⁻¹. The frequencies for the stretching vibration of the terminal C=C bond in alkylacetylenes lie in the 2140-2150 cm⁻¹ interval, the intensities of these bands in the matrix being very low. In the PR spectrum, the band that is closest to this interval is the weak band at 2080 cm⁻¹; in our opinion, this band also characterizes the vibration vC=C. Also characteristic for the ethynyl fragment in the IR spectra of planar molecules are two more intense bands in the 600-700 cm⁻¹ interval, pertaining to in-plane δ CH and outof-plane pCH bending vibrations of the terminal C-H bond. In this interval we have registered strong bands at 686 and 618 cm⁻¹; on the basis of the calculation, these have been assigned



Fig. 2. IR spectra (Ar matrix, 12 K): a) 1,5-hexadiyne, b) products from pyrolysis of 1,5-hexadiyne (B = benzene, F = fulvene, A = allene; plus-sign denotes minor components).

to δ CH and ρ CH, respectively. It should be noted that a band at 620 cm⁻¹ was also observed in [8], but it was not identified because of the low intensity of the spectrum.

Methylene Group. In order to assign the bands that we found in the spectrum to the five vibrations of the methylene group $(2A_1 + B_1 + 2B_2)$, we compared the IR spectrum of the PR with the spectra of alkyl radicals having a terminal radical center: ethyl, propyl, butyl, isobutyl, pentyl, and neopentyl [11, 15]. For all of these radicals, the vibration frequencies for the CH_2 group are characteristic. Thus, the antiphase stretching vibration of C-H bonds is located in the narrow interval 3100-3115 cm⁻¹, and the synphase vibration in the 3015-3035 cm⁻¹ interval. Therefore, the weak bands at 3111 and 3026 cm⁻¹ that are registered in the PR spectrum have also been assigned to v_{as} CH₂ (B₂) and v_{s} CH₂ (A₁), respectively. Of the two bands in the 1350-1450 cm⁻¹ region, we believe that the weak band at 1440 cm⁻¹ corresponds to the scissoring vibration δCH_2 (A₁) (δCH_2 for the radical $CD_3 CH_2$ is 1438 cm⁻¹ [11]). The second, medium-intensity band with a lower wavenumber 1369 cm^{-1} is regarded as an overtone of the most intense band of the PR at 686 cm⁻¹. In the IR spectra of all alkyl radicals with the formula RCH2, the out-of-plane vibration of the CH2 group is characterized by an intense, broad band in the 520-560 cm^{-1} region [11, 15]; therefore, we also consider that the medium-intensity band at 532 cm⁻¹ in the spectrum of the PR pertains to ρCH_2 (B₁). The methylene group rocking vibration band $\delta_r CH_2$ (B₂) should lie in the 900-1100 cm⁻¹ region. In this interval we observe two medium-intensity bands at 1062 and 1017 cm⁻¹; on the basis of our calculations, we assign the first of these bands to $\delta_r CH_2$ and the second to the stretching vibration vC-C (A_1), which should also lie in the 930-1080 cm⁻¹ region, i.e., between the values of $vC \equiv C$ in MA and v_sCCC in allene. Such an assignment of these bands is in

qualitative agreement with the results from an <u>ab initio</u> calculation [7], which approximately predicts the values $\delta_{\rm r}$ CH₂ 1160 cm⁻¹ and vC-C 1072 cm⁻¹ (Table 2). In the opposite case, with assignment of the 1062 cm⁻¹ band to the vC-C vibration in PR, its value, and also the value of the force constant of the C-C bond (≈ 8 mdyn/Å) will be close to the corresponding values in allene ($\nu_{\rm s}$ CCC 1072 cm⁻¹, $F_{\rm C=C} = 8.7$ mdyn/Å [10, p. 259]).

In the region below 500 cm⁻¹, where we should find the in-plane δ CCC (B₂) and out-ofplane ρ CCC (B₁) bending vibrations of the carbon skeleton of the PR, we find a single strong band at 482 cm⁻¹, which we assign to δ CCC. The ρ CCC vibration band, according to the calculation, should lie below 450 cm⁻¹, i.e., beyond the limit of our measurements.

From our analysis we can draw certain conclusions regarding the influence of the unpaired electron on the vibrational spectrum of the PR and on the character of the bonds in this radical. It had been shown previously that delocalization of electron density in the AR [14] and the ethyl radical (ER) [11] leads to substantial changes in the stretching vibration frequencies in the IR spectra of these species in comparison with propylene and ethane, respectively. Thus, in the AR, the vibrations $v_{as}CCC$ 1284 cm⁻¹ and $v_{s}CCC$ 1242 cm⁻¹ are located between vC-C 920 cm⁻¹ and vC=C 1650 cm⁻¹ in propylene, and all of the stretching vibrations vCH lie in the interval 3107-3019 cm⁻¹, i.e., in the region of vibrations of olefin protons. As already noted, in the ER the stretching vibration bands vCH₂ of the methylene group are also above 3000 cm⁻¹ [11], evidently as a consequence of the stronger C-C bond in this radical in comparison with the bond in ethane (vC-C in ER 1138 cm⁻¹ [11]; vC-C in ethane 1016 cm⁻¹ [10, p. 165]).

The PR contains a conjugated system consisting of the half-filled 2p orbital and one of the π orbitals of the triple bond [7], in which delocalization of electron density may take place. And in fact, the values that we established for the stretching vibration frequencies vC=C 2080 cm⁻¹ and vC-C 1017 cm⁻¹ in PR are located (respectively) below and above vC=C 2142 cm⁻¹ and vC-C 930 cm⁻¹ in MA. The calculation shows that the force constant of the triple bond $F_{C=C}$ = 15.05 mdyn/Å in the PR is smaller than $F_{C=C}$ = 15.87 mdyn/Å in MA; in contrast, F_{C-C} = 6.53 mdyn/Å in the radical is greater than $F_{C=C}$ = 5.30 mdyn/Å in MA. In the region of stretching vibrations of C-H bonds, we also observe a decrease in the frequency vCH from 3322 cm⁻¹ in the MA to 3307 cm⁻¹ in the PR, whereas the vibrations $v_{as}CH_2$ 3111 cm⁻¹ and v_sCH_2 3026 cm⁻¹ of the methylene group in the radical lie in the interval characteristic for olefin protons, in contrast to the stretching vibrations of the CH₃ group in MA, which are located below 3000 cm⁻¹. Thus, in the PR there is a certain strengthening of the ordinary carbon-carbon bond and a weakening of the carbon-carbon triple bond, evidently because of delocalization of electron density in the conjugated system of orbitals.

On the basis of the force field that we obtained for the PR (Table 3), we calculated theoretical vibrational spectra for its deuterium-substituted analogs C_3H_2D , C_3D_2H , and C_3D_3 (Table 2), through which we can make an assignment of individual experimental bands for the radicals C_3H_2D and C_3D_3 [8] to normal vibrations; these data should also be of assistance in further interpretation of the spectra of these species.

CONCLUSIONS

1. The propargyl radical, obtained by vacuum pyrolysis of propargyl iodide and dipropargly oxalate, has been stabilized in an argon matrix at 12 K and characterized by IR spectroscopy on the basis of 12 of its absorption bands.

2. The vibration frequencies of the propargyl radical have been calculated theoretically, the observed bands have been assigned to normal vibrations, and the force field of this radical has been determined.

3. The values obtained for the stretching vibration frequencies $vC\equiv C$, vC=C, vCH, and vCH_2 indicate strengthening of the ordinary carbon-carbon bond and weakening of the triple bond in the propargyl radical as a result of electron density delocalization in the conjugated system of orbitals.

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SPATIAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES.

49. VIBRATIONAL SPECTRA, DIPOLE MOMENTS, AND CONFORMATIONS

- OF 2-AROXY-1,3,2-DIOXAPHOSPHEPINES AND THEIR BENZO ANALOGS
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Seven-membered rings with a single planar fragment have a comparatively small set of basis conformations, limited to four structures: chair (C), boat (B), twist (T), and twistboat (TB) [1]. Different forms of the ring are described through the method of Kremer and Pople. Slight changes in the intracyclic bond angles at the P and O atoms lead to the appearance of forms of the ring that differ significantly in torsion angle. The TB_2 form is characterized by near-zero torsion angles along one of the P-O and $C_{\rm SD}^2-C_{\rm SD}^3$ bonds; i.e., the C⁷O¹PO³ and O³C⁴C⁵C⁶ fragments in this form are planar. The change from a benzo fragment to a double bond favors the appearance of a broad set of flexible forms, related to change in geometric parameters of the planar fragment. The puckering parameters and the torsion angles are listed in Table 1. In the series of 4,7-dihydro-1,3,2-dioxaphosphepines (1,3,2-DOP) with three-coordinated phosphorus, the flexible forms [T] (T or TB) are preferred [2-4]. In the 5,6-benzo derivatives, C forms also participate in the equilibrium, along with the flexible forms [2, 4, 5].

Contradictory results have been obtained for the 2-phenoxy derivatives. From an analysis of the ¹H NMR temperature spectra, it follows that 2-phenoxy-1,3,2-DOP (I) is conformationally homogeneous; in view of the 6-Hz difference in values of the vicinal SSCC ³JPOCH for the axial (a) and equatorial (e) protons, the C conformation has been ascribed to this compound; for the benzo analog (II), an equilibrium of the C and T forms is suggested [6]. However, the conclusions drawn in that study did not have an adequate basis and have been subjected to criticism [7]. And indeed, in the example of the 5,6-dichloro derivative (III),

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