IR spectroscopic study of allylperoxy radical and products of its phototransformations in the Ar matrix

E. G. Baskir and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

Matrix IR spectra of an allylperoxy radical (**1**) obtained by co-condensation of allyl radicals and molecular oxygen into an argon matrix at 12 K have been studied. The bands observed in the matrix IR spectrum are assigned to normal vibrations on the basis of *ab initio* calculations of radical **1** and its isotope-substituted analog $C_3H_5{}^{18}O_2$ (**1a**). The band at 1128.6 cm^{-1} is assigned to the stretching vibration of the O—O bond. The products of photodecomposition of radical **1** under UV irradiation (λ > 248 nm) have been studied. A vinylacyl radical (**2**) with a characteristic high vibrational ν(C=O) frequency of 1823.1 cm^{-1} has been observed among the products of photolysis of **1**. According to the data of quantum chemical calculations, some delocalization of a free electron between an oxygen atom and two C atoms is observed in radical **2**.

Key words: allylperoxy radical, vinylacyl radical; pyrolysis, photolysis; matrix isolation; IR spectroscopy; quantum chemical calculations.

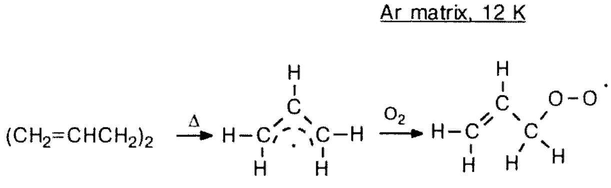
Peroxy radicals play an important role in hydrocarbon oxidation in catalytic and biological processes[1—3] and low-temperature oxidation of organic compounds in upper atmospheric layers.[4] Many works are devoted to spectroscopic studies of peroxy radicals. In particular, the series of alkylperoxy radicals was studied in detail by matrix IR spectroscopy.[5—9] Data on the vibrational spectrum of allylperoxy radical **1** are scarce, although the π-structure of this radical has been established by ESR spectroscopy,[2,10—12] and its behavior in the adamantane matrix has been studied.[12] In addition, the structure of radical **1** and the possibility of oxygen migration in it were studied by the *ab initio* method.[13,14] Attempts to study this radical in the gas phase by mass spectrometry[12] or photoelectron spectroscopy[11] were unsuccessful.

The purpose of this work is the IR spectroscopic study of allyperoxy radical **1** stabilized in an argon matrix and products of its transformations upon UV irradiation.[✦]

Experimental

Allylperoxy radical **1** was obtained by the reaction of an allyl radical, the product of vacuum pyrolysis of 1,5-hexadiene, with molecular oxygen added to a matrix gas (Ar) in a concentration of 2—10 % (Scheme 1).

Scheme 1



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The pyrolysis of the initial 1,5-hexadiene was carried out at ~1100 K and 10^{-4} Torr in a quartz reactor 120 mm in length and 5 mm in diameter attached to an optical helium cryostat. Radicals **1** were formed during the combined deposition of allyl radicals along with an excess of argon (~1 : 1000) containing from 2 to 10 % of O_2 onto the polished surface of a copper cube cooled to 12 K by a Displex 208R cryogenic system (Air Products & Chemicals) with a closed cycle. IR spectra with 1-cm^{-1} resolution were recorded on a Bruker IFS-113v FT-spectrometer by the scheme of beam reflection. Photolysis was carried out by a high-pressure mercury lamp (1000 W) through a window of CaF_2 mounted into a vacuum jacket of the cryostat. Thermal radiation of the lamp was suppressed by a water filter 10 cm in width. The wavelength of UV radiation was varied by 2-mm BS-5 (λ > 320 nm) and BS-12 (λ > 250 nm) glass light filters.

Technical 1,5-hexadiene was used without additional purification.

Isotope-substituted $^{18}O_2$ of 99 % purity with 82 % isotope saturation was used in the experiments.

Quantum chemical calculations were performed according to the GAUSSIAN 92 program[16] at the HF/3-21G and HF/6-31G* levels.

[✦] Preliminary results were presented at the XII International Conference on Physical Organic Chemistry (Padova, Italy) in 1994.[15]

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Results and Discussion

Spectrum of allylperoxy radical. 1,5-Hexadiene was chosen as a source of allyl radicals due to the high selectivity of its thermal decomposition in the gas phase.[17] The reaction between the allyl radical and O_2 was performed with variation of the content of the latter from 1 to 20 % in argon. The presence of ~10 % of O_2 provides almost complete conversion of the allyl radical. The IR spectrum of the forming products (Fig. 1, *a*) contains 26 new bands assigned to an unstable species along with the bands of the initial hexadiene, very weak bands of the allyl radical (801.2 cm^{-1}) and allene (1955.2 and 837.4 cm^{-1}): at 3102.7 (m), 3044.5 (v.w), 3006.0 (m), 2950.6 (m), 1880.2 (w), 1870.1 (w), 1649.8 (m), 1452.6 (m), 1438.4 (m), 1425.4 (m), 1420.3 (s), 1333.3 (m), 1285.3 (w), 1252.5 (m), 1167.4 (m), 1128.6 (m), 1108.6 (m), 1001.8 (s), 999.2 (s sh), 945.9 (m sh), 939.4 (v.s), 935.3 (v.s), 855.8 (s), 850.7 (s), 619.3 (w), and 494.2 (w) cm^{-1}. As should be expected, the intensities of these bands decrease on heating the matrix to 35—37 K, which provides diffusion of particles in the matrix

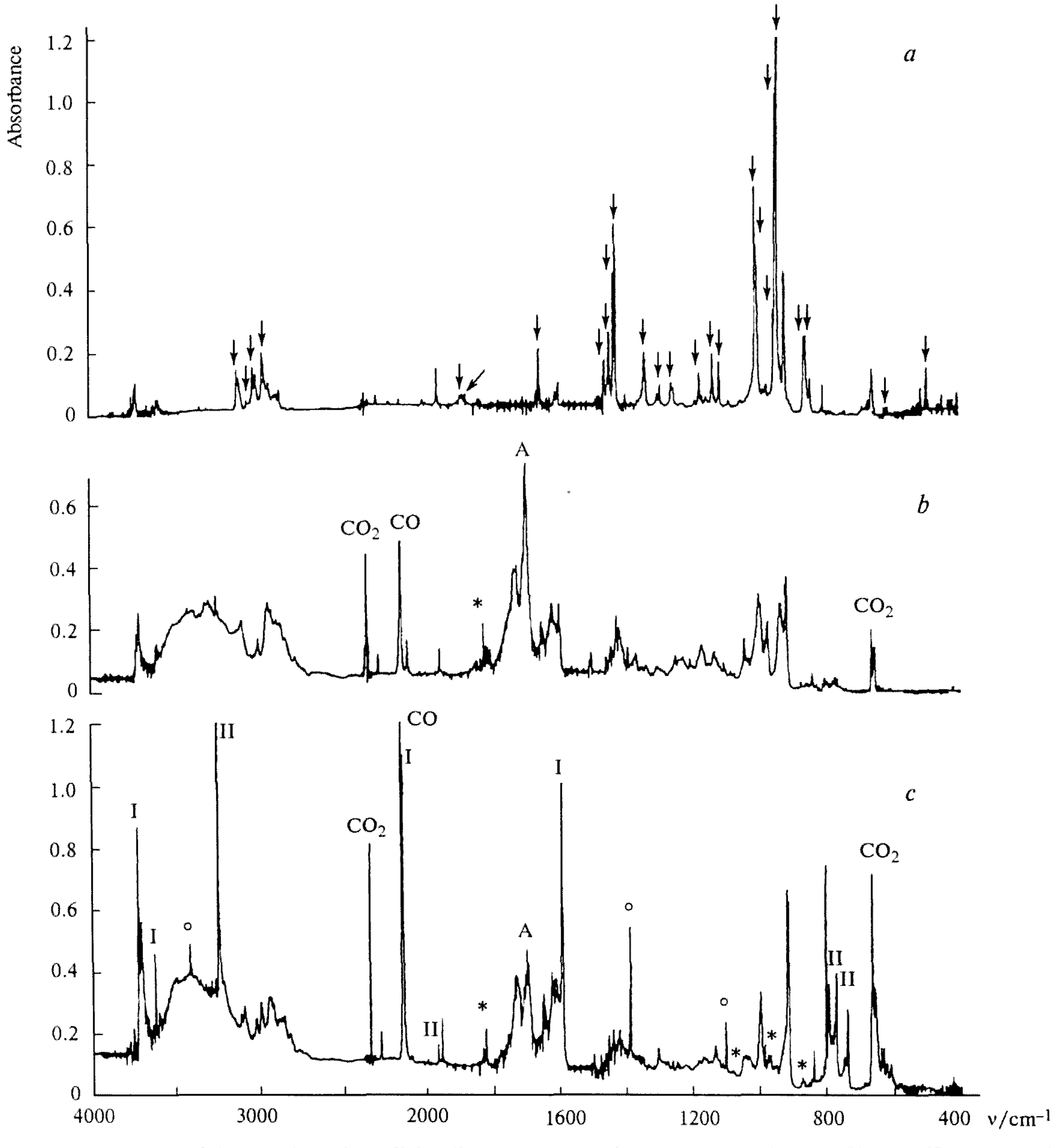
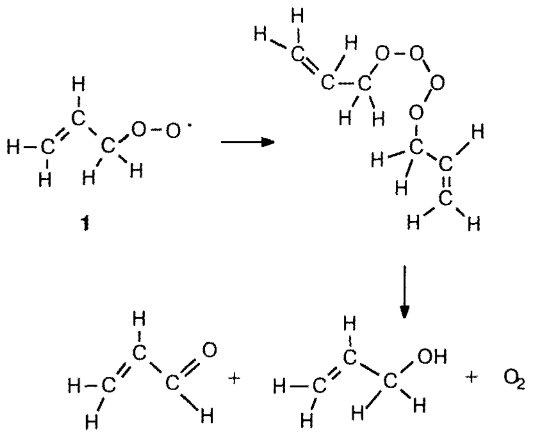


Fig. 1. IR spectra of products of the reaction of an allyl radical with oxygen in an argon matrix at 12 K: *a*, C_3H_5 + (Ar + 8 % of O_2) before photolysis; *b*, C_3H_5 + (Ar + 8 % of O_2) after UV irradiation (λ > 250 nm) of the matrix; *c*, C_3H_5 + (Ar + 3 % of O_2) after UV irradiation (λ > 250 nm) of the matrix. Bands of radical **1** are denoted by arrows; those of radical **2** are denoted by stars; circles indicate bands of an $HO_2^{\cdot}$ radical; letters A designate bands of acrolein; figures I and II indicate bands of $C_2H_2...H_2O$ and $CO...H_2O$ complexes, respectively.

and simultaneous appearance of bands at 1469.5 (m), 1366.5 (w), 1159.0 (m), 1005.0 (s), 988.3 (s), 969.3 (m), 762.3, and 584.0 (w) cm^{-1} that disappear when the matrix is heated to room temperature, recondensed into another tube, and again deposited.

It is known[5–9] that the reaction of alkyl radicals with oxygen results in the formation of alkylperoxy radicals. According to the ESR spectroscopy data,[2,10–12] in the gas phase containing O_2, the allyl radical behaves similarly to form **1**. This allowed us to assign the first set of the bands disappearing on heating the matrix to 35—37 K precisely to radical **1** that is dimerized at this temperature. Such dimer with bridge of four O atoms is labile molecule. Its decomposition at ~300 K results in the extrusion of an O_2 molecule accompanied by disproportionation of peroxy radicals appeared[18] to form aldehyde and alcohol. In fact, the bands of acrolein and allyl alcohol are observed in the spectra of the products of complete thaw out of the matrix followed their repeat deposition onto the copper substrate (Scheme 2). The same products were detected by GC-MS analysis of the mixture obtained.

Scheme 2



The IR bands observed in the spectra were assigned to normal vibrations of the allylperoxy radical on the basis of the experimental results obtained, *ab initio* and semiempirical quantum chemical calculations performed, and comparison with the literature data for similar in structure alkylperoxy radicals,[5–9] alkenes,[19,20] and allyl alcohol[21] (Table 1).

According to the data of the quantum chemical calculations,[13,14] the structure of radical **1** is nonplanar and belongs to symmetry group C_1. The calculated IR spectrum of this structure exhibits 24 normal vibrations, three of which are related to twisting and bending vibrations of the H_2COO moiety usually absorb at frequencies lower than 400 cm^{-1} and are beyond measurement limits.

Four bands of radical **1** were observed in the range of stretching vibrations of C—H bonds (3150—2900 cm^{-1}). The bands at 3102.7 and 3000.6 cm^{-1} are assigned to the asymmetric $\nu_{as}(=CH_2)$ and symmetric $\nu_s(=CH_2)$ stretching vibrations of C—H bonds in the terminal CH_2 group, respectively (in the spectrum of allyl alcohol, the bands at 3100 and 2996 cm^{-1} correspond to these vibrations).[21] The band at 3044.5 cm^{-1} belongs to the vibration of the CH moiety, while the absorption at 2950.6 cm^{-1} is attributed to the asymmetric stretching vibration of the C—H bonds of the peroxy moiety. It is likely that the band of the symmetric vibration appeared at frequencies lower than 2900 cm^{-1} is low intense and has not been detected.

The band with a maximum at 1649.8 cm^{-1} corresponds to the stretching $\nu(C=C)$ vibration. Although this band coincides with the absorption band of propylene (1649.5 cm^{-1}), a decrease in its intensity upon both heating the matrix or photolysis proves that it belongs to radical **1**. The band at 1167.4 cm^{-1} is assigned to the stretching vibration of the ordinary C—C bond. However, according to the results of the calculations, this vibration is not characteristic and can contribute into the vibrations with absorption in the range of 940 cm^{-1} (939.4 and 935.3 cm^{-1}).

The medium intense bands at 1420.3, 1001.8, and 999.2 cm^{-1} probably related to the scissor $\delta(=CH_2)$, rocking $\delta_r(=CH_2)$, and twisting $\rho_t(=CH_2)$ vibrations, respectively, were assigned to bending vibrations of the methylene moiety in radical **1** as well as one of the most intense bands at 939.4 cm^{-1} belonging to the nonplanar wagging $\rho_w(=CH_2)$ vibration. The bands at 1285.3 and 619.3 cm^{-1} correspond to planar and nonplanar bending vibrations of the CH moiety, respectively. The bands at 1474, 1351, 1242, and 800 cm^{-1} in the spectrum of the ethylperoxy radical[8] correspond to bending vibrations of the CH_2 group of the peroxy moiety. Therefore, the absorption bands at 1452.6, 1333.3, 1252.5, and 935.3 cm^{-1} are assigned to similar vibrations in radical **1**. Weak signals at 1880.2 and 1870.1 cm^{-1} in the spectrum of radical **1** likely belong to overtones of $2\rho_w(=CH_2)$ (939.4 cm^{-1}) and $2\delta_r(CH_2)$ (935.3 cm^{-1}) vibrations. It is noteworthy that all the aforementioned bands remain almost unchanged or change only slightly on going to the spectrum of isotope-substituted radical **1a**.

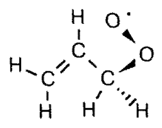
The bands that are considerably shifted in the spectrum of heavier radical **1a** and related to the vibrations of the C—O—O moiety are of special interest (Fig. 2, *a*, *b*). The 1130—1000 cm^{-1} range is typical of stretching vibrations $\nu(O—O)$ of the O—O bond of these radicals. In this range, two bands of medium intensity at 1128.6 and 1108.6 cm^{-1} were observed. They shift to 1067.6 and 1052.7 cm^{-1}, respectively, in the spectrum of isotope-substituted radical **1a**. The shifting coefficients $\nu(^{16}O_2)/\nu(^{18}O_2)$ of these bands are 1.057 and 1.053, respectively, which is close to the theoretical value of the ratio ($\nu(^{16}O_2)/\nu(^{18}O_2)$ = 1.061), and confirms the presence of the C—O—O moiety in this radical. The bands at 1112 and 1101 cm^{-1} correspond to this vibration in the spectra of alkylperoxy radicals $EtO_2^{\cdot}$ (Ref. 8) and $Pr^iO_2^{\cdot}$ (Ref. 7), respectively. The existence of the

Table 1. Comparison of experimental and calculated frequencies of the vibrational spectrum of the allylperoxy radical

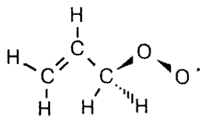
Number of vibration	Assignment	ν/cm^{-1}					
		Experiment		Calculations^a			
				A		B	
		$C_3H_5O_2$	$C_3H_5{}^{18}O_2$	$C_3H_5O_2$	$C_3H_5{}^{18}O_2$	$C_3H_5O_2$	$C_3H_5{}^{18}O_2$
1	$\nu_{as}(=CH_2)$	3102.7	3102.4	3039.3	3039.3	3040.3	3040.3
2	$\nu_s(CH)$	3044.5	3044.5	2989.1	2989.1	2982.5	2982.5
3	$\nu_s(=CH_2)$	3006.0	3006.5	2965.8	2965.8	2965.7	2965.7
4	$\nu_{as}(CH_2)$	2950.6	2950.3	2953.1	2953.0	2945.7	2945.7
5	$\nu_s(CH_2)$	—	—	2898.5	2898.5	2897.2	2897.1
	$2\rho_w(=CH_2)$	1880.2	1880.2				
	$2\delta_r(CH_2)$	1870.1	1870.0				
6	$\nu(C=C)$	1649.8	1649.3	1659.5	1659.5	1625.9	1625.8
7	$\delta(CH_2)$	1452.6	1451.2	1455.4	1455.1	1455.4	1455.1
	?	1438.4	1437.7				
8	$\delta(=CH_2)$	1425.4	1425.1	1423.2	1422.9		
		1420.3	1419.6			1420.8	1420.5
9	$\rho_w(CH_2)$	1333.3	1330.2	1350.0	1348.9	1347.5	1345.9
10	$\delta(CH)$	1285.3	1285.3	1275.1	1274.6	1268.2	1267.6
11	$\rho_{tw}(CH_2)$	1252.5	1247.0	1265.8	1259.3	1261.9	1256.3
12	$\nu(C{-}C)$	1167.4	1166.2	1153.5	1150.5	1146.0	1140.9
13	$\nu(OO)$	**1128.6**^{b}	**1067.6**^{b}	**1131.1**^{b}	**1074.8**^{b}		
		1108.6^b	**1052.7**^{b}			**1120.9**^{b}	**1068.3**^{b}
14	$\delta_r(=CH_2)$	1001.8	1001.4	1018.2	1017.9	1015.5	1014.0
15	$\rho_t(=CH_2)$	999.2	999.2	976.9	976.2	984.7	976.6
		945.9	943.0			974.7	972.4
16	$\rho_w(=CH_2)$	939.4	940.4	971.8	959.4		
17	$\delta_r(CH_2)$	935.3	935.3	932.5	927.7	931.5	921.0
18	$\nu(CO)$	**855.8**^{b}	**844.2**^{b}			**885.6**^{b}	**881.2**^{b}
		850.7^b	**837.9**^{b}	**877.7**^{b}	**871.5**^{b}		
19	$\rho_w(CH)$	619.3	618.8	656.6	648.4	641.7	635.1
20	$\delta(COO)$	494.2	479.7	507.0	496.2	481.7	468.0
21	$\delta(CCC)$	—	—	369.7	365.4	407.8	404.7
22	$\delta(CCO)$	—	—	312.6	305.4	309.1	303.2
23	$\rho_t(HCCO)$	—	—	112.1	109.3	116.6	112.4
24	$\rho_t(CCCO)$	—	—	80.9	79.2	83.9	83.0

[a] The frequencies were calculated in the 6-31G* basis (with a scaling factor of 0.89). [b] The most characteristic bands.

two bands belonging to the ν(O—O) vibration in the spectrum of the radical can likely be explained by the fact that this moiety exists as two conformers. In fact, according to the *ab initio* calculation, radical **1** can exist as two forms (**A** and **B**) with almost equal energies $E_A \approx E_B \approx -266.083$ au and differing by some rotation of the O atom around the C—O bond.



A



B

The calculations of the vibrational spectrum (see Table 1) have confirmed the possibility of some differences in the frequency values of these conformers, which makes it possible to assign the doublet of bands at 855.8 and 850.7 cm^{-1}, which shift to 844.2 and 837.9 cm^{-1} in the spectrum of isotope-substituted radical **1a**, to the stretching ν(C—O) vibration. The bands at 902, 838, and 789 cm^{-1} in the spectra of the alkylperoxy $MeO_2^{\cdot}$ (Ref. 5), $EtO_2^{\cdot}$ (Ref. 8), and $Pr^iO_2^{\cdot}$ (Ref. 7) radicals, respectively, correspond to the same vibration. The band at 494.2 cm^{-1}, which shifts to 479.7 cm^{-1} in the spectrum of radical **1a**, is assigned to the bending δ(COO) vibration. This shift and position of the band agree well

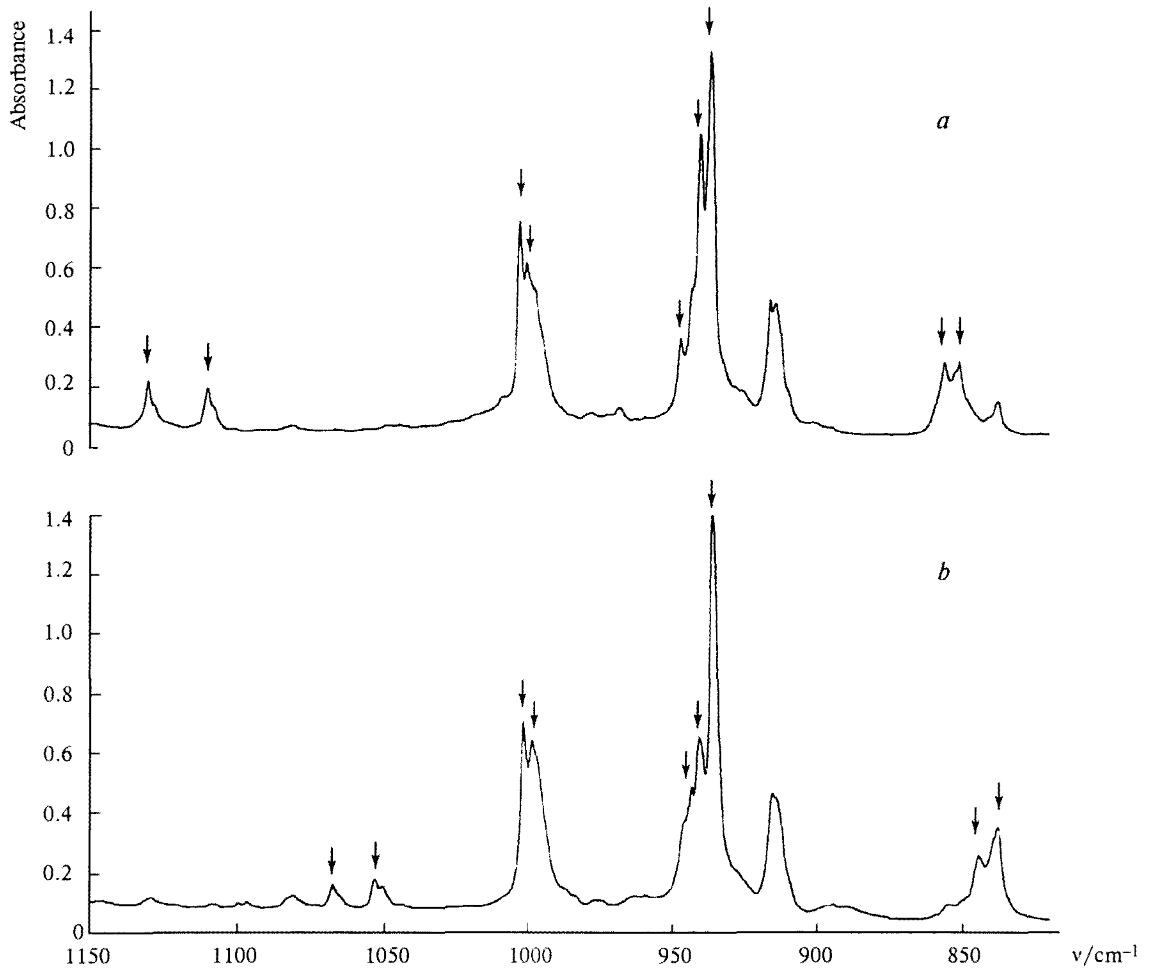
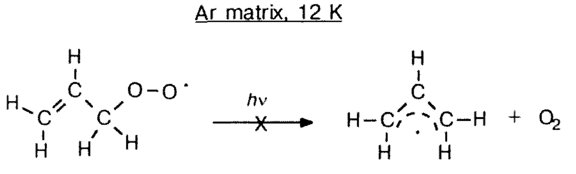


Fig. 2. IR spectra of products of the reaction of an allyl radical and oxygen in an argon matrix at 12 K in the range of 1150—820 cm^{-1}: *a*, C_3H_5 + (Ar + 8 % of $^{16}O_2$); *b*, C_3H_5 + (Ar + 8 % of $^{18}O_2$). Bands of radicals **1** (*a*) and **1a** (*b*) are denoted by arrows.

with the IR spectroscopy data[8] for the $EtO_2^{\cdot}$ radical: 499 cm^{-1} ($\delta C^{16}O^{16}O$) and 484 cm^{-1} ($\delta C^{18}O^{18}O$).

Photolysis of allyperoxy radical. UV irradiation (λ > 320 nm) of the matrix with stabilized radical **1** results in a decrease in the intensity of its bands and their complete disappearance upon UV irradiation with λ > 250 nm (see Fig. 1, *b*). At the same time, several bands belonging to photodecomposition products appeared in the spectrum.

Contrary to the predictions of the calculations[13] about a low stability of the C—O bond in radical **1**, no products of its decomposition *via* this bond cleavage to form allyl radicals were observed.



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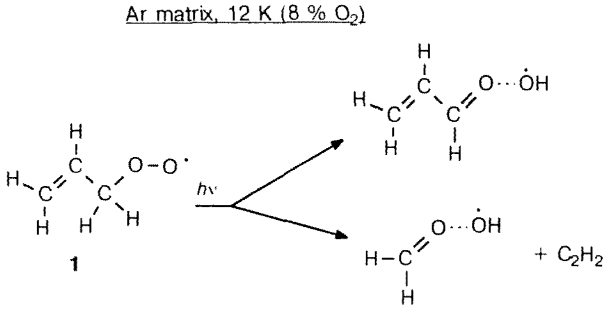
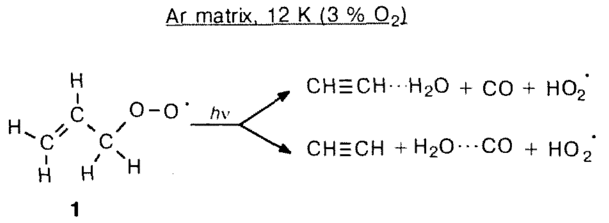
The signals belonging to CO (2142.5 cm^{-1}), H_2O (3704.6 and 3601.7 cm^{-1}), C_2H_2 (3287.1 and 736.4 cm^{-1}), and O_3 (1040.4 and 1036.8 cm^{-1}) can be distinguished in all of the spectra of photolysis products. However, it should be mentioned that the compositions of photolysis products differ depending on the content of O_2 in the matrix. Irradiation of the matrices obtained by co-condensation of pyrolysis products with an argon mixture containing ~8—10 % of O_2 results in the appearance of rather intense bands at 1731 and 1697 cm^{-1} (1694 and 1667 cm^{-1} for isotope-substituted radical **1a**, respectively) in the spectrum. The positions of these bands and their shifts due to isotope substitution allow one to suppose that they belong to probable decomposition products, formaldehyde and acrolein, whose spectra exhibit absorption bands at 1746 and 1723 cm^{-1}, respectively.[19] Their broadening and low-frequency shift can be explained by the formation of their complexes with the $OH^{\cdot}$ radical rather than formation of individual molecules. An analogous effect was observed in the spectra of aldehydes formed upon photolysis of alkylperoxy radicals[5—9] (Scheme 3).

Scheme 3



The decomposition of products occurs *via* the different pathways upon the photolysis of the matrices obtained by deposition of an Ar mixture containing 2—3 % of O_2 (Scheme 4). The spectrum (see Fig. 1, *c*) contain the bands assigned to the $HO_2^{\cdot}$ radical (3412.2, 1388.5, and 1100.7 cm^{-1} or 3399.4, 1379.5, and 1038.7 cm^{-1} for the isotope-substituted radical)[22] and the signals that can be assigned to CO...H_2O (3723.2, 3623.1, 2148.1, and 1591.7 cm^{-1} or 3709.9, 3615.6, 2100.0, and 1585.7 cm^{-1} for the isotope-substituted radical)[23] and C_2H_2...H_2O (3242.9, 1968.0, 792.6, and 782.7 cm^{-1})[24] complexes.

Scheme 4



The appearance of a new band at 1823.1 cm^{-1} is of the most interest. This band is very sensitive to matrix conditions, *i.e.*, it appears as a single band only in the case of a more rigid matrix containing ~2—3 % of O_2 (Fig. 3, *a*). An increase in the content of O_2 results in the appearance of additional weak bands at 1815.4, 1810.1, and 1803.1 cm^{-1} (Fig. 3, *b*), which retained on heating the matrix to the temperature of diffusion (Fig. 3, *c*). The band at 1823.1 cm^{-1} was observed at the very beginning of photolysis, and then its intensity remained almost unchanged. In the spectrum of photolysis products of isotope-substituted radical **1a** (Fig. 3, *d*), this band shifts to 1788.9 cm^{-1}, which testifies that a new particle contains the acyl C=O moiety. Although the band that characterizes a similar vibration is localized, as a rule, at lower frequencies in spectra of ordinary carbonyl compounds (in the 1700—1750 cm^{-1} range[19]), the increase in its frequency to 1828—1875 cm^{-1} is typical of acyl radicals.[26—29] It can be assumed that the band observed belongs to a new unstable particle,

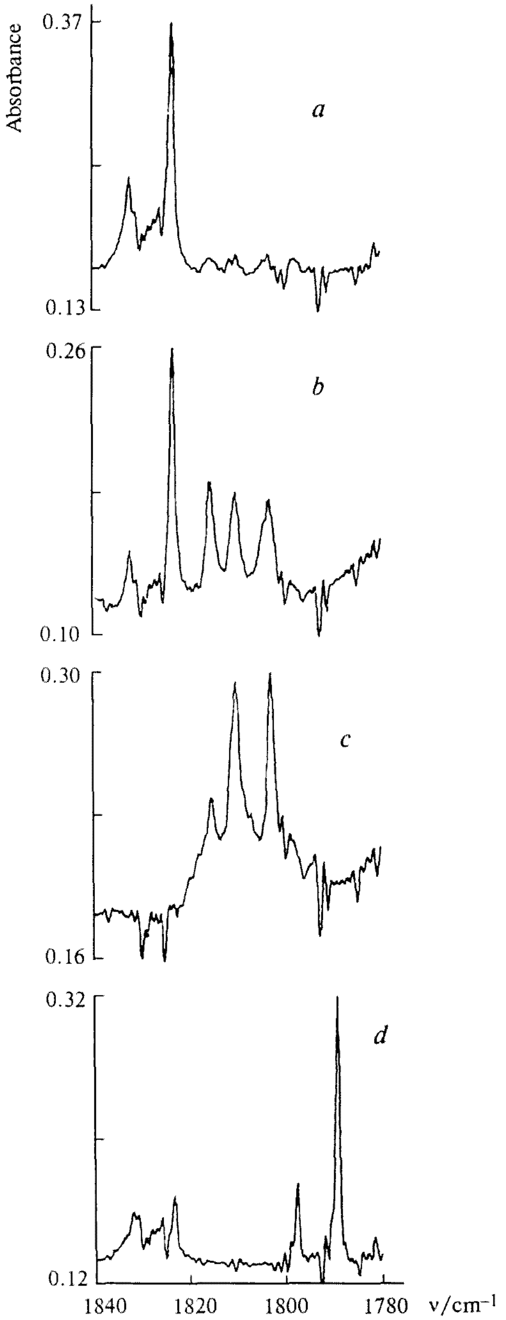
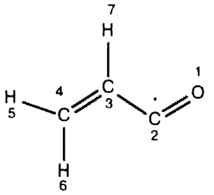


Fig. 3. IR spectra of products of the reaction of an allyl radical with oxygen in an argon matrix at 12 K in the range of 1840—1780 cm^{-1} after photolysis: *a*, C_3H_5 + (Ar + 3 % of O_2); *b*, C_3H_5 + (Ar + 8 % of O_2) before heating; *c*, C_3H_5 + (Ar + 8 % of O_2) after heating the matrix to 35 K; *d*, C_3H_5 + (Ar + 3 % of $^{18}O_2$).

Table 2. Charge distribution, spin density, and calculated structural parameters in the vinylacyl radical[a]

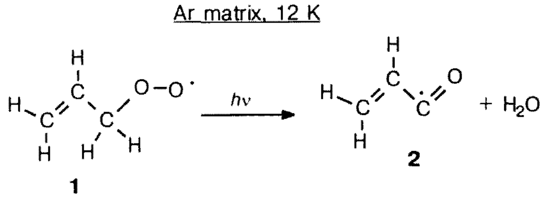


Atom	Charge distribution[b]	Spin density[b]	Structural parameters	
			Bond (d/Å)	Angle (ω/deg)
O(1)	−0.429	0.269	O(1)=C(2) (1.167)	C(2)—C(3)—O(1) (128.8)
C(2)	+0.376	0.651	C(2)—C(3) (1.481)	C(3)—C(4)—C(2) (120.4)
C(3)	−0.252	0.468	C(3)=C(4) (1.330)	H(5)—C(4)—C(3) (121.6)
C(4)	−0.337	−0.458	C(4)—H(5) (1.074)	H(6)—C(4)—C(3) (121.2)
H(5)	+0.207	0.029	C(4)—H(6) (1.075)	H(7)—C(3)—C(2) (117.1)
H(6)	+0.211	0.035	C(3)—H(7) (1.077)	
H(7)	+0.224	0.006		

[a] Calculated by the *ab initio* method in the 6-31 G* basis. [b] In fractions of the electron charge.

vinylacyl radical **2** formed due to the elimination of a water molecule from radical **1** (Scheme 5).

Scheme 5



In the spectrum of photolysis products, several additional weak bands appeared and disappeared simultaneously with the band at 1823.1 cm^{-1} (1832.0, 1094.4, 975.3, and 870.7 cm^{-1} or 1797.3, 1094.4, 975.4, and 868.3 cm^{-1} for isotope substitution) and probably related to radical **2**.

The energy of radical **2** and its structure were calculated by the *ab initio* quantum chemical method (Table 2). According to the results of the calculations, radical **2** has a planar structure and can exist as two conformers, and the *trans*-configuration is by ~6 kJ mol^{-1} more favorable than the *cis*-form. In addition, the calculations testifies that there is some delocalization of a free electron between the O atom and two C atoms in the vinylacyl radical.

The assignment of the spectral bands observed to normal vibrations of radical **2** and comparison with the calculated data are presented in Table 3. The most intense band at 1823.1 cm^{-1} is assigned to the stretching ν(C=O) vibration of the radical with *trans*-configuration, while the weaker band at 1832.0 cm^{-1} is assigned to ν(C=O) of the *cis*-conformer. It is likely that the bands that are retained in the range of 1800 cm^{-1} on heating belong to stable products of dimerization or the reaction of the radical with O_2. Very weak bands at 1094.4, 975.3, and 870.7 cm^{-1} can be assigned to bending vibrations of CH_2 or CH moieties. Unfortunately, the other signals of radical **2** were not reliably identified because of overlapping with bands of other products.

The high value (1823.1 cm^{-1}) of the frequency of the stretching ν(C=O) vibration in the radical compared to that of the similar vibration in acrolein (1728 cm^{-1})[19]

Table 3. Comparison of experimental and calculated frequencies of the vibrational spectrum of the vinylacyl radical

Number of vibration	Assignment	ν/cm^{-1}	
		Experiment	Calculations[a]
1	$\nu_{as}(=CH_2)$	—	3059.5
2	$\nu_s(CH)$	—	2987.7
3	$\nu_s(=CH_2)$	—	2975.8
4	$\nu(C=O)$	**1832.0**[b]	
		1823.1[b]	**1886.6**[b]
5	$\nu(C=C)$	—	1498.5
6	$\delta(CH_2)$	—	1341.2
7	$\delta(CH)$	—	1209.9
8	$\delta_r(CH_2)$	1094.4	1072.6
12	$\rho_t(CH_2)$	975.3	983.7
13	$\rho_w(CH_2)$	870.7	965.7
9	$\nu(CC)$	—	847.3
14	$\rho_w(CH)$	—	629.8
10	$\delta(CCC)$	—	517.8
11	$\delta(CCO)$	—	296.3
15	$\rho_t(CCCO)$	—	160.7

[a] Calculated in the 6-31G* basis (with a scaling factor of 0.89). [b] The most characteristic bands.

testifies that the C=O bond becomes stronger. This is confirmed by the calculations, according to which the corresponding bond in the radical shortens from 1.189 to 1.167 Å. This band is localized at somewhat lower frequency than the band of the similar vibration in the spectra of formyl (1863 cm^{-1})[26] and acetyl (1875 cm^{-1})[29] radicals. At the same time, it is close to the value of ν(C=O) recently obtained for the benzoyl radical (1828 cm^{-1}) by the fast scanning IR spectroscopy method,[28] which can be explained by the coupling of a free electron with the C=C bond of the vinyl moiety or with the benzene ring.

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