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Infrared Spectrum of the Formylperoxy Radical in Solid Argon

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Infrared spectra and frequency assignments of various isotopomers of formylperoxy radical HC(O)OO in solid argon are presented. The formylperoxy radical was produced through the discharge production of formyl radical followed by the association reaction of formyl radicals with molecular oxygen in solid argon. Quantum chemical calculations indicate that the observed spectrum can be assigned to formylperoxy radical with the O−O bond in a cis position relative to the C−H bond.

Introduction

Formyl radical HCO is a very important intermediate species that participates in many chemical reactions, such as the combustion of hydrocarbons and the photochemistry of the atmosphere. The kinetics and chemistry associated with formyl radical have been reported. The reaction between HCO and O_2 is one such study, which is thought to produce HO_2 + CO and OH + CO_2.[1−4] The HO_2-forming process was directly confirmed by laser magnetic resonance spectroscopic experiments.[5] Ab initio Hartree−Fock calculations suggested that the reaction of HCO with O_2 proceeded through the formation of a formylperoxy radical, HC(O)OO.[6] When initially formed, the formylperoxy radical was highly excited: the initial internal energy for the formylperoxy radical cannot be deactivated rapidly enough to stabilize the radical with respect to dissociation in the gas phase.

Matrix isolation provides a powerful method for trapping reactive intermediates and free radicals. In a low temperature solid matrix, the reaction can be very effectively quenched after the primary reaction or, at most, the earliest stages of the overall process. Transient reaction intermediates, which fragment readily in the gas phase, can be stabilized with removal of the internal thermal energy when they are trapped in the matrix environment.[7] Lee and co-workers suggested the formation of the HC(O)OO formylperoxy radical in studies of the photochemical oxidation of formaldehyde in solid O_2 at 13 K.[8,9] Two infrared absorptions at 1790 and 1089.9 cm^{-1} have been assigned to the C═O and C−O stretching vibrations of the HC(O)OO radical. However, as the authors pointed out, it is probable that the observed frequencies may not be those of isolated formylperoxy radical, since the radical could be either complexed to or perturbed by the cage partner HO_2.[8,9] In this paper, we report the infrared absorption spectrum of the isolated formylperoxy radical produced by the association reaction between HCO radical and molecular oxygen in solid argon. The HCO radical was formed by co-deposition of CH_3OH/Ar with high frequency discharged O_2/Ar mixture.

Experimental and Theoretical Methods

The formylperoxy radical was prepared by condensation of CH_3OH/Ar and O_2/Ar via high-frequency discharge. The experimental setup for high-frequency discharge and matrix isolation Fourier transform infrared (FTIR) spectroscopic investigation has been described in detail previously.[10] Briefly, two separated gas streams containing O_2/Ar and CH_3OH/Ar were co-deposited onto a 4 K CsI window simultaneously for 2−4 h at a rate of 3−5 mmol/h. One of the gas streams was subjected to discharge from a Tesla coil. The tip of the Tesla coil was connected to a copper cap on one end of a quartz tube extending into the vacuum chamber. The other end of the quartz tube was connected to a copper tube with ground potential. Discharge takes place between the cap and the copper tube. Infrared spectra were recorded on a Bruker Equinox 55 spectrometer at 0.5 cm^{-1} resolution using a DTGS detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broad-band irradiation using a high-pressure mercury arc lamp. The CH_3OH/Ar (1:1000 to 1:2000) and O_2/Ar (1:100 to 1:200) mixtures were prepared in a stainless steel vacuum line using standard manometric technique. CH_3OH was cooled to 77 K using liquid N_2 and evacuated to remove volatile impurities. Isotopically labeled samples $^{18}O_2$ (Cambridge Isotope Laboratories, 99%), CD_3OD (Merck, 99%), and $^{13}CH_3OH$ and $CH_3{}^{18}OH$ (99%, Cambridge Isotopic Laboratories) and selected mixtures were also prepared to elucidate the effects of isotopic substitution on the vibrational spectra of the reaction products.

Quantum chemical calculations were performed using the Gaussian 98 program.[11] The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang, and Parr was utilized (B3LYP).[12,13] Additional comparison ab initio calculations were also done using the second-order Moller−Plesset perturbation theory (MP2) as well.[14] The 6-311++G** basis sets were used.[15,16] The geometries were fully optimized; the harmonic vibrational frequencies were calculated with analytic second derivatives, and zero point vibrational energies (ZPVE) were derived.

Results and Discussion

Low power microwave or radio frequency discharges have often been used in matrix isolation spectroscopic studies.[7,17] Free radicals are formed and trapped by co-condensation of the argon beam passed through the discharge with the precursor molecules. The power level of discharge can control the fragmentation of the precursor molecules to some extent. In the present experi-

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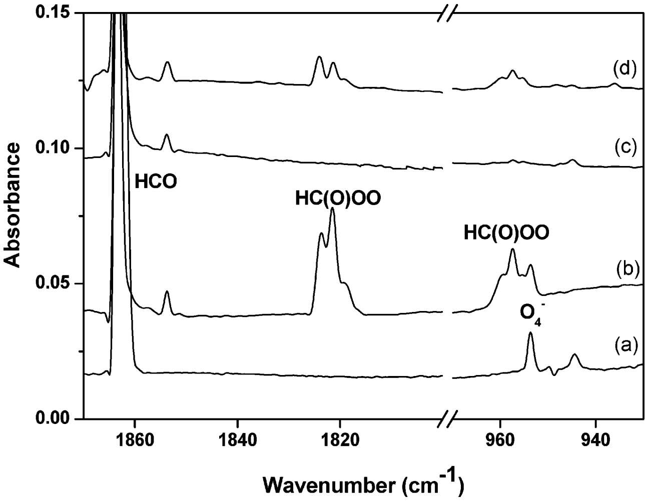

Figure 1. Infrared spectra in 1870−1800 and 970−930 cm^{-1} regions from co-deposition of 0.05% CH_3OH/Ar and discharged 0.5% O_2/Ar at 4 K. (a) After 120 min deposition, (b) after 25 K annealing, (c) after 20 min broad-band irradiation, and (d) after 30 K annealing.

ments, CH_3OH was used as the precursor molecule. Condensation of CH_3OH/Ar with discharged Ar at 4 K resulted in fragmentation of CH_3OH to CH_2OH (1182.7 and 1047.5 cm^{-1}),[18] H_2CO (1742.1 cm^{-1}), HCO (1863.4 and 1084.8 cm^{-1}),[19] and CO. The relative intensities of these fragments depend on the power level of discharge. Generally, the formation of CH_2OH dominated at low power level of discharge, while CO and HCO became the major fragments when relatively high level power was employed. These fragment absorptions remained almost unchanged on subsequent annealing to 25 and 30 K. The CH_2OH and HCO absorptions markedly decreased on broad-band irradiation. Similarly, O_3 (1039.4 cm^{-1}), O_3^- (803.9 cm^{-1}),[20] O_4^- (953.6 cm^{-1}),[21] and O_4^+ (1118.4 cm^{-1})[22] were produced after discharge of O_2/Ar and condensation at 4 K. The O_3 and O_3^- absorptions increased whereas the O_4^- and O_4^+ absorptions decreased on annealing. All these oxygen cluster absorptions were eliminated on broad-band irradiation.

New absorptions were observed when CH_3OH/Ar was co-deposited with discharged O_2/Ar. Figure 1 shows the spectra in the 1870−1800 and 970−930 cm^{-1} regions from co-deposition of 0.05% CH_3OH/Ar with discharged 0.5% O_2/Ar. Besides the above-mentioned absorptions, HOO (3412.1, 1388.3, and 1100.7 cm^{-1})[23] and $ArHAr^+$ (903.0 cm^{-1})[24] absorptions were observed after sample deposition. Annealing to 25 K (Figure 1b) markedly decreased the HCO absorptions and produced new 1821.5 and 957.3 cm^{-1} absorptions, with little effect on the other absorptions such as HOO, CH_2OH, and H_2CO. The 1821.5 and 957.3 cm^{-1} bands virtually disappeared on broad-band irradiation (Figure 1c), and slightly regenerated on further annealing to 30 K (Figure 1d).

Experiments were repeated with the $^{13}CH_3OH/O_2$, $CH_3{}^{18}OH/O_2$, CD_3OD/O_2, $CH_3OH/{}^{18}O_2$, $^{12}CH_3OH$ + $^{13}CH_3OH/O_2$, $CH_3{}^{16}OH$ + $CH_3{}^{18}OH/O_2$, and $CH_3OH/{}^{16}O_2$ + $^{18}O_2$ samples. The new product infrared absorptions using these isotopic samples are listed in Table 1. The infrared spectra in selected regions using different isotopic samples are shown in Figures 2 and 3.

TABLE 1: Infrared Absorptions (cm^{-1}) Observed for Various HC(O)OO Isotopomers in Solid Argon

	C=O[a]	C−O
HCOOO	1821.5	957.3
$H^{13}COOO$	1783.7	938.7
$HC^{18}OOO$	1782.5	953.8
$HCO^{18}O^{18}O$	1816.9	933.6
$HCO^{18}OO$		936.7
$HCOO^{18}O$		955.3
DCOOO	1775.2	

[a] The C=O stretching frequencies of $HC(O)^{18}OO$ and $HC(O)O^{18}O$ cannot be resolved.

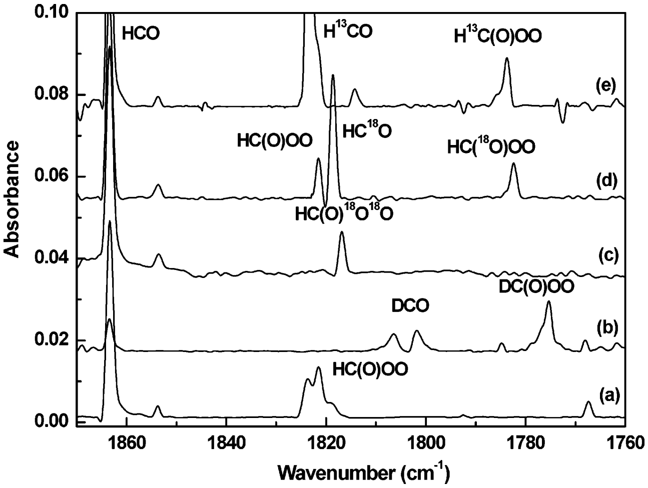

Figure 2. Infrared spectra in 1870−1760 cm^{-1} region from co-deposition of CH_3OH/Ar and discharged O_2/Ar at 4 K. Spectra were taken after 25 K annealing. (a) 0.05% CH_3OH + 0.5% O_2, (b) 0.05% CD_3OD + 0.5% O_2, (c) 0.05% CH_3OH + 0.5% $^{18}O_2$, (d) 0.03% $CH_3{}^{16}OH$ + 0.03% $CH_3{}^{18}OH$ + 0.5% O_2, and (e) 0.02% $^{12}CH_3OH$ + 0.04% $^{13}CH_3OH$ + 0.5% O_2.

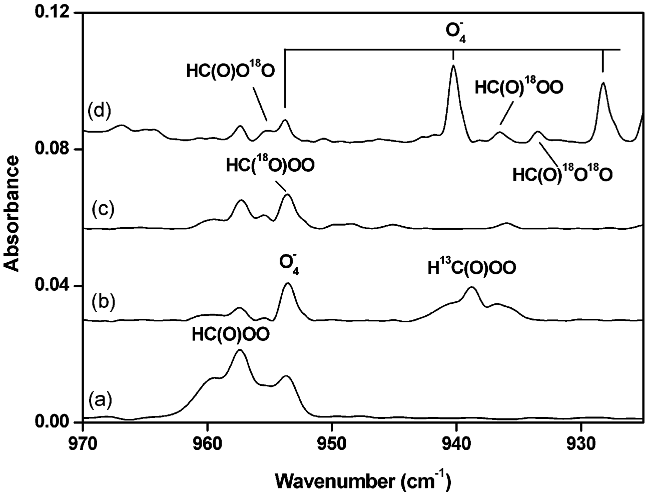

Figure 3. Infrared spectra in 970−925 cm^{-1} region from co-deposition of CH_3OH/Ar and discharged O_2/Ar at 4 K. Spectra were taken after 25 K annealing. (a) 0.05% CH_3OH + 0.5% O_2, (b) 0.02% $^{12}CH_3OH$ + 0.04% $^{13}CH_3OH$ + 0.5% O_2. (c) 0.03% $CH_3{}^{16}OH$ + 0.03% $CH_3{}^{18}OH$ + 0.5% O_2, and (d) 0.05% CH_3OH + 0.4% $^{16}O_2$ +0.4% $^{18}O_2$.

The 1821.5 and 957.3 cm^{-1} bands appeared together on annealing, and can be grouped together by their consistent behavior upon annealing and broad-band irradiation, which suggests different vibrational modes of the same molecule. These two bands were appeared in the experiments when CH_3OH/Ar was co-deposited with discharged O_2/Ar sample. The same absorptions were produced when CH_3OH/Ar was subjected to discharge and co-deposited with O_2/Ar. The 1821.5 and 957.3 cm^{-1} absorptions appeared on annealing, during which the HCO absorptions markedly decreased. The intensities of these two bands strongly depended on the HCO absorptions. They were weak in the low power level discharge experiments, in which the HCO absorptions were weak. These observations suggest

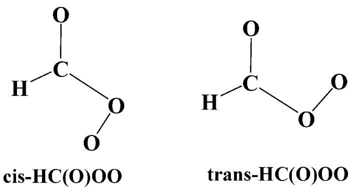
cis-HC(O)OO **trans-HC(O)OO**

Figure 4. Structures of the formylperoxy radical HC(O)OO.

that the new product species were formed by the reaction of HCO, which was produced from CH_3OH during sample deposition. The 1821.5 cm^{-1} band exhibited a very small shift when $CH_3OH/^{18}O_2$ sample was employed in the experiment, but shifted to 1783.7 cm^{-1} with $^{13}CH_3OH/O_2$, to 1782.5 cm^{-1} with $CH_3{}^{18}OH/O_2$, and to 1775.2 cm^{-1} with CD_3OD/O_2. The isotopic frequency ratios of 1.0212 for $^{12}CH_3OH/^{13}CH_3OH$ and 1.0219 for $CH_3{}^{16}OH/CH_3{}^{18}OH$ are very similar to those of the C═O stretching vibration of the HCO molecule ($H^{12}CO/H^{13}CO$, 1.0219; and $HC^{16}O/HC^{18}O$, 1.0246), which indicates that the 1821.5 cm^{-1} band is due to a C═O stretching vibration. In the mixed $^{12}CH_3OH + {}^{13}CH_3OH/O_2$ and $CH_3{}^{16}OH + CH_3{}^{18}OH/O_2$ experiments, only the pure isotopic counterparts were presented in the spectra (Figure 2), indicating that only one HCO subunit is involved in the new species and that the HCO subunit came from the CH_3OH precursor. The 957.3 cm^{-1} band showed a very small shift (3.5 cm^{-1}) with the $CH_3{}^{18}OH/O_2$ sample. This mode was observed at 938.7 cm^{-1} in the $^{13}CH_3OH/O_2$ experiment. In the mixed $^{12}CH_3OH + {}^{13}CH_3OH/O_2$ and $CH_3{}^{16}OH + CH_3{}^{18}OH/O_2$ experiments, no obvious intermediate components were observed, suggesting that one C atom and one O atom that contributed from the CH_3OH precursor are involved in this mode. When a $CH_3OH/^{18}O_2$ sample was used, the band was observed at 933.6 cm^{-1}. The $^{16}O_2/^{18}O_2$ isotopic frequency ratio of 1.0254 and the $^{12}C/^{13}C$ isotopic frequency ratio of 1.0198 imply that this band is a C−O stretching vibration. In the mixed $CH_3OH/^{16}O_2 + {}^{18}O_2$ experiment, a quartet at 957.3, 955.3, 936.7, and 933.6 cm^{-1} was observed, indicating that two inequivalent oxygen atoms are involved in this vibration, and that these two oxygen atoms came from the oxygen molecule. These isotopic substitution experiments confirmed that the new product species involves one HCO subunit and one O_2 subunit with two inequivalent O atoms, and was produced by the reaction of HCO with O_2 in solid argon. Accordingly, we assign the 1821.5 and 957.3 cm^{-1} bands to the C═O and C−O stretching vibrations of the formylperoxy HC(O)OO radical.

Quantum chemical computations were performed to support the experimental assignment and to provide insight into the geometry and electronic structure in HC(O)OO. Two stable structural isomers—a trans and a cis form so labeled depending upon the O−O bond geometry with respect to the C−H bond—were found on the doublet potential energy surface as shown in Figure 4, and the optimized geometric parameters and vibrational frequencies and intensities are listed in Table 2. As can be seen, excellent agreement was found between the B3LYP hybrid density functional theory and the second-order Moller−Plesset perturbation theory. These calculations indicated that both the trans and cis isomers have a doublet ground state with a planar structure and are very close in energy. The cis form was predicted to be more stable than the trans form by about 2.0 kcal/mol at B3LYP/6-311++G** level and 1.9 kcal/mol at MP2/6-311++G** level. The optimized bond lengths of the cis and trans structures are very similar, with only about 0.001−0.002 Å differences. Both structural isomers have $^2A''$ ground state with the unpaired electron occupying the 3a″ molecular orbital which is largely antibonding p_π orbital of the O_2 subunit.

TABLE 2: Calculated Structures (Bond Lengths in Å, Bond Angles in deg), Vibrational Frequencies (cm^{-1}), and Intensities (km/mol) for *cis*- and *trans*-HC(O)OO

	cis-HC(O)OO		*trans*-HC(O)OO	
	B3LYP	MP2	B3LYP	MP2
R(C═O)	1.179	1.185	1.178	1.186
R(C−H)	1.099	1.099	1.097	1.096
R(C−O)	1.428	1.427	1.428	1.423
R(O−O)	1.328	1.315	1.326	1.319
∠COO	111.0	110.1	114.1	112.9
∠O═CO	119.9	120.2	125.3	125.6
∠HC═O	130.4	130.4	129.2	129.1
C−H str	3053.7(14)	3118.1(13)	3070.0(24)	3140.5(24)
C═O str	1888.2(280)	1884.8(286)	1878.3(245)	1868.3(230)
HCO in-plane bend	1334.5(0)	1334.5(0)	1361.9(0)	1392.4(0)
O−O str	1145.4(26)	1205.1(86)	1100.5(46)	1128.8(123)
HCO out-of -plane bend	1009.3(0)	1023.4(0)	975.4(0)	999.3(0)
C−O str	953.3(226)	987.8(308)	865.1(176)	905.4(227)
COO in-plane bend	586.2(16)	602.6(16)	776.6(39)	803.5(17)
	404.3(16)	420.1(15)	322.6(3)	334.8(3)
	175.5(19)	178.1(17)	244.4(18)	246.0(17)

As listed in Table 2, the calculated vibrational frequencies and intensities of the two HC(O)OO structural isomers are quite different. For the cis structure, the C═O and C−O stretching vibrations were predicted to be at 1887.9 and 955.6 cm^{-1} with 280 and 226 km/mol IR intensities at B3LYP/6-311++G** level. MP2/6-311++G** calculations gave frequencies of 1884.8 and 987.7 cm^{-1} with 287 and 308 km/mol IR intensities. These two modes were predicted to have the largest IR intensities at both levels of theory. There are nine vibrational modes for the formylperoxy radical. Besides the C═O and C−O stretching modes, the other modes such as C−H stretching (14 km/mol) and O−O stretching (26 km/mol) modes were predicted to have much lower IR intensities than the C═O and C−O stretching modes. For the trans isomer, the C═O and C−O stretching modes were predicted at 1879.5 and 864.6 cm^{-1} with 245 and 176 km/mol IR intensities by B3LYP, and at 1868.3 and 905.4 cm^{-1} with 230 and 228 km/mol intensities using MP2. Although the calculated C═O stretching frequencies of the cis and trans isomers are very close and both fit the experimental value very well, there is 91 (B3LYP) or 82.3 cm^{-1} (MP2) difference between the C−O stretching frequencies of the two isomers. The predicted C−O stretching frequency of the cis structure is only about 1.7 cm^{-1} lower with B3LYP or 30.4 cm^{-1} higher with MP2, whereas the frequency of the trans structure is about 92.7 (B3LYP) or 51.9 cm^{-1} (MP2) lower than the experimentally observed value of 957.3 cm^{-1}. Due mainly to the neglect of anharmonicity, computed vibrational frequencies are generally higher than the experimental values. Apparently the calculated frequencies of the cis structure fit the experimental values much better than that of the trans structure. These indicate that the experimentally observed HC(O)OO radical has a cis structure. The same conclusion can also be deduced from the relative stability prediction as has already been mentioned. As listed in Table 3, the calculated isotopic frequency shifts of the cis structure are in good agreement with the experimental values.

According to our calculations, the trans structure is stable; however, no spectroscopic evidence was found for the trans structure. Although the trans and cis isomeric forms are similar in energy, they are separated by a calculated potential energy barrier of 8.4 kcal/mol (cis to trans) with B3LYP. No indication

TABLE 3: Comparison between Observed and Calculated Isotopic Frequency Differences (cm^{-1}) for the Product Molecules

	C═O		C−O	
	calcd	obsd	calcd	obsd
HCOOO	0.0	0.0	0.0	0.0
$H^{13}COOO$	40.5	37.8	20.3	18.6
$HC^{18}OOO$	42.9	39.0	2.0	3.5
$HCO^{18}O^{18}O$	0.7	4.6	22.0	23.7
$HCO^{18}OO$	0.5		17.9	20.6
$HCOO^{18}O$	0.2		3.4	2.0
DCOOO	58.9	46.3	20.0	

of a possible IR-induced conformational process was observed during FTIR measurements.

It has been reported that formylperoxy radical, HC(O)OO, was isolated in solid O_2 at 13−18 K from the UV photoexcitation of solid O_2/H_2CO and O_2/*trans*-$H_2C_2O_2$ samples, respectively.[8,9] The key mechanistic step for the formation of HC(O)OO was thought to involve the intermediacy of the photochemically generated HCO radical which reacted with molecular O_2. Two absorptions at 1790.0 and 1089.9 cm^{-1} were assigned to the C═O and C−O stretching vibrations of the formylperoxy radical in solid O_2. The C═O stretching frequency is 31.5 cm^{-1} lower while the C−O stretching frequency is 132.6 cm^{-1} higher than those of present argon matrix values. Such large frequency differences cannot be due to matrix shifts in solid argon and oxygen. The matrix shifts in solid argon are expected to be similar to the matrix shifts in solid O_2. As a reference point, the C═O stretching of H_2CO was observed at 1740.0 and 1742.1 cm^{-1} in solid O_2 and argon, respectively. Our argon matrix isolated values clearly indicate that the formylperoxy radical observed in solid O_2 is not an “isolated” molecule. As the authors already pointed out, the observed absorptions may be due to a formylperoxy−hydroperoxy radical complex rather than a matrix isolated formylperoxy radical. The observation of different frequencies for the O_2/D_2CO and O_2/HDO samples also suggested the complex assignment in solid O_2.[8,9] The C═O stretching band of *cis*-HC(O)OO shows strong splitting similar to HArF, a molecule which exhibits strong dipoles.[25] The dipole moment of the formylperoxy radical was predicted to be only 1.7 D. A different matrix environment may be responsible for the band structure of the formylperoxy radical.

The present isotopic substitution experiments showed that the formylperoxy radical was formed by the reaction of formyl radical with O_2 in solid argon, reaction 1:

$$HCO(^2A') + O_2(^3\Sigma_g^-) \rightarrow HC(O)OO(^2A'') \qquad \Delta E = -29.4 \text{ kcal/mol} \quad (1)$$

, which was predicted to be exothermic by about 29.4 kcal/mol at B3LYP/6-311++G** level. The HC(O)OO absorptions increased on annealing, indicating that the association reaction (1) requires negligible activation energy. The HC(O)OO absorptions were eliminated on broad-band irradiation, during which the CO and CO_2 absorptions increased. It appears that UV−visible light initiates dissociation reactions to form CO and CO_2.

Conclusions

The formylperoxy radical HC(O)OO has been studied by matrix isolation infrared absorption spectroscopy and quantum chemical calculations. The formylperoxy radical was produced by the association reaction between HCO radical and molecular oxygen in solid argon. The HCO radical was formed by codeposition of CH_3OH/Ar with a high frequency discharged O_2/Ar mixture. On the basis of the isotopic substitution experiments, absorptions at 1821.5 and 957.3 cm^{-1} are assigned to the C═O and C−O stretching vibrations of the formylperoxy radical with the O−O bond in a cis position relative to the C−H bond.

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