Inorg. Chem. **2005**, *44*, 4415–4420

Inorganic Chemistry
Article

Properties of Chloroformyl Peroxynitrate, $ClC(O)OONO_2$

Plácido García,[†] Holger Pernice,[†] Helge Willner,*[,†] Heinz Oberhammer,*[,‡] and Gustavo A. Argüello[§]

FB C, Anorganische Chemie, Bergische Universität Wuppertal, Gaussstrasse 20,
D-42097 Wuppertal, Germany, Institut für Physikalische und Theoretische Chemie der Universität
Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany, and Departamento de
Físico-Química, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina

Received February 14, 2005

The synthesis of $ClC(O)OONO_2$ is accomplished by photolysis of a mixture of Cl_2, NO_2, and CO in large excess of O_2 at about –70 °C. The product is isolated after repeated trap-to-trap condensation. The solid compound melts at –84 °C, and the extrapolated boiling point is 80 °C. $ClC(O)OONO_2$ is characterized by IR, Raman, ^{13}C NMR, and UV spectroscopy. According to the IR matrix spectra, the compound exists at room temperature only as a single conformer. The molecular structure of $ClC(O)OONO_2$ is determined by gas electron diffraction. The molecule possesses a gauche structure with a dihedral angle of $\phi(COON) = 86.7(19)°$, and the C═O bond is oriented syn with respect to the O–O bond. The short O–O bond (1.418(6) Å) and the long N–O bond (1.511(8) Å) are consistent with the facile dissociation of $ClC(O)OONO_2$ into the radicals ClC(O)OO and NO_2. The experimental geometry of $ClC(O)OONO_2$ is reproduced reasonably well by B3LYP/6-311+G(2df) calculations, whereas the MP2 approximation predicts the N–O bond considerably too long and the dihedral angle too small.

Introduction

Organic peroxynitrates ($ROONO_2$) have been extensively studied due to their importance in atmospheric chemistry. The most abundant acetyl peroxynitrate (PAN) was already detected in the atmosphere in 1956[1] as one of the products in photo smog formation in urban environments.[2,3] Organic $ROONO_2$ species are formed in atmospheric degradation of hydrocarbons according to eqs 1−3.

$$RH + OH \rightarrow R + H_2O \qquad (1)$$

$$R + O_2 \ (+ M) \rightarrow RO_2 \ (+M) \qquad (2)$$

$$RO_2 + NO_2 \ (+ M) \rightarrow RO_2NO_2 \ (+M) \qquad (3)$$

Less abundant are fluorinated peroxynitrates resulting from the atmospheric depletion of CFC replacements. The most important examples are CF_3OONO_2,[4,5] $CF_3C(O)OONO_2$,[6−8] $CF_3OC(O)OONO_2$,[9] and $FC(O)OONO_2$,[10] which have been well characterized and are thermally quite stable. Very few chlorinated peroxynitrates have been investigated so far.[6]

Oxidation reactions in the troposphere are mainly driven by the OH radical; nevertheless the Cl atom chemistry is also considered to be of importance.[11−16] In polluted areas containing CO, NO_x, and NaCl sea aerosols, formation of

---

* To whom correspondence should be addressed. E-mail: willner@uni-wuppertal.de (H.W.); heinz.oberhammer@uni-tuebingen.de (H.O.).

[†] Bergische Universität Wuppertal. Fax: +49 (0) 202-439 3052.

[‡] Universität Tübingen. Fax: +49 (0) 7071-29 5490.

[§] Universidad Nacional de Cordoba. Fax: +54 351 433 4188.

(1) Stephens, E. R.; Hanst, P. L.; Doerr, R. C.; Scott, W. E. *Ind. Eng. Chem.* **1956**, *48*, 1498−1504.

(2) Nieboer, H.; van Ham, J. *Atmos. Environ.* **1976**, *10*, 115−120.

(3) Darley, E. F.; Kettner, K. A.; Stephens, E. R. *Anal. Chem.* **1963**, *35*, 589−591.

(4) Hohorst, F. A.; DesMarteau, D. D. *Inorg. Chem.* **1974**, *13*, 715−719.

(5) Kopitzky, R.; Willner, H.; Mack, H. G.; Pfeiffer, A.; Oberhammer, H. *Inorg. Chem.* **1998**, *37*, 6208−6213.

(6) Zabel, F.; Kirchner, F.; Becker, K. H. *Int. J. Chem. Kinet.* **1994**, *26*, 827−845.

(7) Wallington, T. J.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **1994**, *226*, 563−569.

(8) Hermann, A.; Niemeyer, J.; Mack, H. G.; Kopitzky, R.; Beuleke, M.; Willner, H.; Christen, D.; Schäfer, M.; Bauder, A.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 1672−1676.

(9) von Ahsen, S.; Garcia, P.; Willner, H.; Argüello, G. A. *Inorg. Chem.*, submitted.

(10) Scheffler, D.; Schaper, I.; Willner, H.; Mack, H. G.; Oberhammer, H. *Inorg. Chem.* **1997**, *36*, 339.

(11) Andersen, M. P. S.; Hurley, M. D.; Wallington, T. J.; Ball, J. C.; Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Nielsen, O. J. *Chem. Phys. Lett.* **2003**, *379*, 28−36.

(12) McFiggans, G.; Cox, R. A.; Mössinger, J. C.; Allan, B. J.; Plane, J. M. C. *J. Geophys. Res. [Atmos.]* **2002**, *107*, ACH10/1−ACH10/13.

(13) Wenger, J. C.; Le Calvé, S.; Sidebottom, H. W.; Wirtz, K.; Reviejo, M. M.; Franklin, J. A. *Environ. Sci. Technol.* **2004**, *38*, 831−837.

(14) Le Crane, J. P.; Villenave, E.; Hurley, M. D.; Wallington, T. J.; Nishida, S.; Takahashi, K.; Matsumi, Y. *J. Phys. Chem. A* **2004**, *108*, 795−805.

(15) Taniguchi, N.; Wallington, T. J.; Hurley, M. D.; Guschin, A. G.; Molina, L. T.; Molina, M. J. *J. Phys. Chem. A* **2003**, *107*, 2674−2679.

(16) Tanaka, P. L.; Allen, D. T.; Mullins, C. B. *J. Geophys. Res. [Atmos.]* **2003**, *108*, ACH 4/1−ACH 4/11.

10.1021/ic050229l CCC: $30.25

chloroformyl peroxynitrate, ClC(O)OONO$_2$, is anticipated. The kinetics of the Cl + CO reaction has been studied under atmospheric conditions,[17−19] and the oxidation of CO to CO$_2$ involves the ClC(O)OO radical as the key intermediate.[17] This important radical was recently identified by IR matrix spectroscopy.[20] It plays a role in the upper Venus atmosphere, where CO$_2$ is photodissociated by the strong solar ultraviolet radiation. The observed CO and O$_2$ concentration is much lower than predicted, because the oxidation of CO with O$_2$ is catalyzed by the ClC(O)OO radical.[21,22]

In laboratory experiments ClC(O)OONO$_2$ has been identified as an oxidation product of chlorinated organic compounds and as the principal product of the ultraviolet irradiation of Cl$_2$, NO$_2$, and CO mixtures in air.[23] The compound was characterized in the gas phase by a few IR bands as well as its unimolecular dissociation kinetics. Due to the relatively high thermal stability of ClC(O)OONO$_2$, reported in a recent compilation,[24] it should be present in the tropospheric boundary layer.

The aim of this study is to prepare pure ClC(O)OONO$_2$ and to investigate its physical, spectroscopic, and structural properties.

Experimental Section

CAUTION! Chloroformyl peroxynitrate is potentially explosive, especially in the presence of organic materials. It is important to take appropriate safety precautions, and ClC(O)OONO$_2$ should be handled only in millimolar quantities.

Apparatus and Synthesis. Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (MKS Baratron 221 AHS-1000 and 221 AHS-10, Wilmington, MA), three U-traps, valves with PTFE stems (Young, London, U.K.), and several standard ground joints (NS 14.5). The vacuum line was connected to a 5 L glass photoreactor via a flexible stainless steel tube and to an IR gas cell (optical path length 200 mm, with 0.5 mm thick Si wafers as windows) in the sample compartment of the FTIR instrument. This arrangement made it possible to follow the course of the reaction during the synthesis (by sampling small amounts from the photoreactor) and to monitor, at a later stage, the improvement in the purification process. The product was stored in glass ampules under liquid nitrogen. The ampules were opened and flame-sealed by means of an ampule key.[25]

The synthesis of ClC(O)OONO$_2$ was carried out by photolysis of a mixture of Cl$_2$, NO$_2$, CO, and O$_2$ (all gases standard grade were obtained from Messer, Germany) in a ratio of 1:1:10:50 inside a 5 L round-bottom flask. The photolysis device consisted of a 250 W halogen lamp (Osram Halolux, Munich, Germany) surrounded by a water-jacketed glass tube in the middle of the flask. The flask was placed in a big stainless steel Dewar vessel and was cooled to about −70 °C with ethanol and dry ice. Into the evacuated photoreactor amounts of 1 mmol of NO$_2$ and Cl$_2$ were introduced together with 10 and 50 mmol of CO and O$_2$, respectively. After about 4 h of photolysis, the NO$_2$ was quantitatively consumed and the concentration of CO$_2$ increased rapidly due to oxidation of CO catalyzed by chlorine. The course of the reaction was monitored by FTIR spectroscopy by taking small samples of the gaseous mixture from time to time and checking the growing absorptions of ClC(O)OONO$_2$ (at 1012.3 cm^{-1}) and CO$_2$ (667 cm^{-1}) as well as the decreasing band of NO$_2$ (1617 cm^{-1}). After 4 h of photolysis, all NO$_2$ was consumed and subsequently the content of the reactor was slowly passed using dynamic vacuum through U-traps held at −196 °C to gather all condensable products. The crude product of several batches was then purified by fractional condensation, in three U-traps held at −60, −90, and −196 °C. The content of the traps at −60 and −90 °C was then repeatedly fractionated until a pure ClC(O)OONO$_2$ sample was obtained in the −90 °C trap. At −196 °C, CO$_2$ and small amounts of Cl$_2$CO, ClNO$_2$, and Cl$_2$ were found as byproducts, identified through FTIR spectroscopy by their known spectra and chlorine by its characteristic yellow color. The yield of ClC(O)OONO$_2$ was about 85% related to NO$_2$.

Instrumentation. (a) Vibrational Spectroscopy. IR spectra in the range 4000−400 cm^{-1} of gaseous samples were measured with an FTIR spectrometer (400D, Nicolet, Madison, WI) with an optical resolution of 2 cm^{-1}, and 32 scans were co-added for each spectrum.

The matrix infrared spectra of ClC(O)OONO$_2$ were recorded with a Bruker IFS 66v/S FTIR instrument in reflectance mode using a transfer optic. A DTGS detector and a KBr/Ge beam splitter were used in the 4000−400 cm^{-1} region. Sixty-four scans were added for each spectrum using an apodized resolution of 1 or 0.25 cm^{-1}. Details of the matrix apparatus have been described elsewhere.[26] For the matrix measurements a small amount of pure ClC(O)OONO$_2$ (ca. 0.1 mmol) was kept in a small U-trap at −196 °C and mounted in front of the matrix support. The trap was allowed to reach a temperature of −110 °C, while a gas stream (2 to 4 mmol h^{-1}) of either argon or neon was directed over the solid ClC(O)OONO$_2$, and the resulting gas mixture was condensed on the matrix support at 15 or 6 K, respectively. During matrix deposition the spray-on nozzle in front of the matrix support was heated to different temperatures.

FT-Raman spectra of a solid ClC(O)OONO$_2$ sample at −196 °C were measured in the region 3000−50 cm^{-1} with a FT Raman spectrometer (RFS 100/S, Bruker, Germany) using the 1064 nm excitation line (500 mW) of a Nd:YAG laser. The sample was condensed as a spot on a nickel plated copper finger kept at −196 °C in high vacuum. The solid sample was then excited with the laser through a quartz window. For each spectrum, 128 scans were co-added with a resolution of 4 cm^{-1}.

(b) NMR Spectroscopy. The ^{13}C NMR spectrum of a neat sample was measured using CD$_2$Cl$_2$ as external standard. The sample was vacuum transferred into a 5 mm o.d. NMR tube provided with a rotationally symmetrical PTFE valve.[27] The ^{13}C spectrum was recorded with a Bruker Avance 300 spectrometer at −50 °C with a multinuclear probe head operating at 75.47 MHz.

(c) UV Spectroscopy. UV spectra of ClC(O)OONO$_2$ were recorded at room temperature with a Perkin-Elmer Lambda 900

---

(17) Hewitt, A. D.; Brahan, K. M.; Boone, G. D.; Hewitt, S. A. *Int. J. Chem. Kinet.* **1996**, *28*, 763−771.

(18) Nicovich, J. M.; Kreutter, K. D.; Wine, P. H. *J. Chem. Phys.* **1990**, *92*, 3539−3544.

(19) Clark, T. C.; Clyne, M. A. A.; Stedman, D. H. *Trans. Faraday Soc.* **1966**, *62*, 3354−3365.

(20) Pernice, H.; Garcia, P.; Willner, H.; Francisco, J. S.; Mills, F. P.; Allen, M.; Yung, Y. L. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 14007−14010.

(21) Yung, Y. L.; Demore, W. B. *Icarus* **1982**, *51*, 199−247.

(22) Krasnopolsky, V. A.; Parshev, V. A. *Nature* **1981**, *292*, 610−613.

(23) Spence, J. W.; Edney, E. O.; Hanst, P. L. *Chem. Phys. Lett.* **1978**, *56*, 478−483.

(24) Kirchner, F.; Mayer-Figge, A.; Zabel, F.; Becker, K. H. *Int. J. Chem. Kinet.* **1999**, *31*, 127−144.

(25) Gombler, W.; Willner, H. *J. Phys. E: Sci. Instrum.* **1987**, *20*, 1286−1288.

(26) Schnöckel, H.; Willner, H. In *Infrared and Raman Spectroscopy, Methods and Applications*; Schrader, B., Ed.; VCH: Weinheim, 1994; p 297.

(27) Gombler, W.; Willner, H. *Int. Lab.* **1984**, *14*, 84−85.

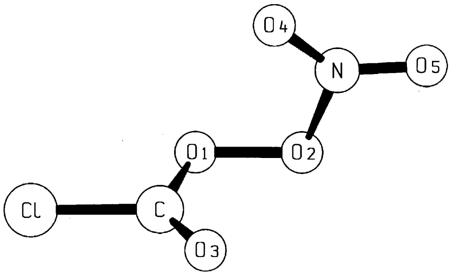


Figure 1. Molecular structure of $ClC(O)OONO_2$ with atom numbering.

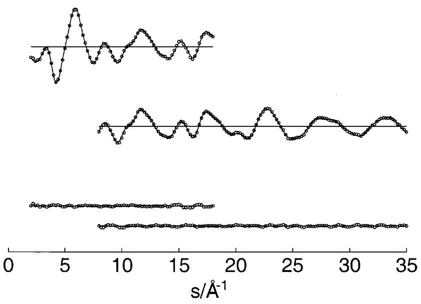


Figure 2. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

spectrometer (Perkin-Elmer, Wellesley, MA) with a resolution of 1 nm. Different amounts of the sample were transferred into a glass cell of 10 cm optical path length equipped with SUPRASIL windows. The absorption cross sections (on base e) were calculated by means of the equation $\sigma = 31.79TAp^{-1}d^{-1}$, where σ is the cross section in 10^{-20} cm^2, T the temperature in K, A the absorbance, p the gas pressure in mbar, and d the optical path length in cm.

(d) Vapor Pressure. The vapor pressure of the neat sample was measured in a small vacuum line equipped with a capacitance manometer (MSK Baratron, AHS-100), the sample reservoir, and a connecting tube to an IR gas cell. The temperature of the sample reservoir was adjusted with a series of ethanol cold baths and measured with a Pt-100 resistance thermometer. At the constant temperatures the resulting vapor pressures were determined. Occasionally, the gas phase was checked through its IR spectrum. Only little decomposition (<1%) was detected at temperatures above 10 °C. During recording of the vapor pressures, the melting point of $ClC(O)OONO_2$ in the reservoir was determined.

(e) Quantum Chemical Calculations. Geometry optimizations were performed for the two possible conformers with syn and anti orientation of the C=O bond with respect to the O−O bond. The MP2 approximation and B3LYP method with 6-311+G(2df) basis sets were applied. According to these calculations the anti conformer is higher in energy by 3.25 (MP2) and 3.02 kcal/mol (B3LYP), respectively. Vibrational amplitudes and corrections were derived from a calculated (B3LYP/6-31G*) force field with the method of Sipachev.[28−30] Calculated geometric parameters and vibrational amplitudes of the syn form are listed together with the experimental values (see below). All quantum chemical calculations were performed with the GAUSSIAN 03 program set.[31]

(f) Electron Diffraction Experiments. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[32] at two nozzle-to-plate distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The compound was kept at −21 °C during the experiment, and the inlet system and gas nozzle were at room temperature. The photographic plates (KODAK Electron Image plates 13 × 18 cm) were analyzed with an Agfa Duoscan HiD scanner, and total scattering intensity curves were obtained with the program SCAN3.[33] Averaged experimental molecular intensities in the s ranges 2−18 and 8−35 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} ($s = (4\pi/\lambda)(\sin\theta/2)$, λ is the electron wavelength, and θ is the scattering angle) are shown in Figure 2

Results and Discussion

Synthesis of $ClC(O)OONO_2$. The Synthesis of $ClC(O)OONO_2$ in neat form is accomplished by photolysis of a mixture of Cl_2, CO, NO_2, and O_2 at −70 °C with subsequent purification of the product by trap-to-trap condensation. The reaction is started by photolytic formation of Cl atoms which react in turn with CO and O_2 (eqs 4 and 5).

$$Cl + CO\ (+M) \rightleftharpoons ClCO\ (+ M) \tag{4}$$

$$ClCO + O_2\ (+M) \rightarrow ClC(O)OO\ (+ M) \tag{5}$$

A low reaction temperature and a high excess of O_2 are needed to yield ClC(O)OO radicals in sufficient concentration. At room temperature, equilibrium 4 is mainly shifted to the left side,[17] and only at low temperatures is the ClCO radical long-lived enough to react with the excess of molecular oxygen.[17,19] The reaction is terminated by recombination of the peroxy radical with NO_2.

$$ClC(O)OO + NO_2\ (+M) \rightleftharpoons ClC(O)OONO_2(+M) \tag{6}$$

Some competing reactions are

$$2ClC(O)OO \rightarrow 2ClC(O)O + O_2 \tag{7}$$

$$ClC(O)O \rightarrow Cl + CO_2 \tag{8}$$

$$ClCO + Cl_2 \rightarrow COCl_2 + Cl \tag{9}$$

Reactions 7 and 8 lead to an increased formation of CO_2 which is observed when no more NO_2 is present.

Once the peroxynitrate is formed, it is relatively stable and can be handled in a vacuum line at room temperature. The half-lives at 298.4 and 293.7 K are 33 and 61 min, respectively.[23] The activation energy for the cleavage of the

---

(28) Sipachev, V. A. *J. Mol. Struct. (THEOCHEM)* **1985**, *121*, 143.

(29) Sipachev, V. A. *Adv. Mol. Struct. Res.* **1999**, *5*, 263.

(30) Sipachev, V. A. *NATO Sci. Ser., II* **2002**, *68*, 73.

(31) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S. Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, revision B.04; Gaussian Inc.: Pittsburgh, PA, 2003.

(32) Oberhammer, H. In *Molecular Structure by Diffraction Methods*; The Chemical Society London: London, 1976; Vol. 4, p 24.

(33) Atavin, E. G.; Vilkov, L. V. *Instrum. Exp. Tech.* **2002**, *45*, 754−757.

Table 1. Vibrational Wavenumbers (cm^{-1}) and Band Intensities for ClC(O)OONO$_2$

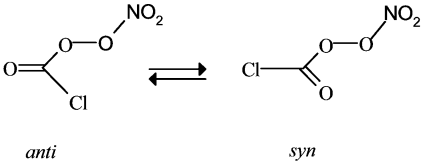
IR (gas)	I^a	Ne^b	I^a	Raman	calcd^c (rel int)	assignment/description mode	
3034	2.3	3033.8	2.4			$\nu_2 + \nu_3$	
2017	3.0	2023.3	2.9			$2\ \nu_4$	
1842	50	1841.9	57	1823 w	1890.6 (65)	ν_1	ν(C=O)
1756	77	1755.9	90	1734 w	1819.3 (90)	ν_2	$\nu_{as}(NO_2)$
1299	41	1303.6	54	1295 m	1348.3 (51)	ν_3	$\nu_s(NO_2)$
1013	100	1009.3	100	1008 vw	996.6 (100)	ν_4	ν(C−O)
977	7.4	974.7	11			$\nu_{10} + \nu_{14}$	
905	3.6	909.6	5.6	906 s	953.3 (10)	ν_5	ν(O−O)
863	7.7	862.3	9.4	864 m	868.2 (8.4)	ν_6	δ(O−C=O)
790	38	786.9	29	790 w	803.5 (46)	ν_7	$\delta(NO_2)$
714	0.8	711.9	2.0	713 vw	733.9 (1.8)	ν_8	oop NO$_2$
669	3.5	672.6	2.1	646 w	681.5 (3.3)	ν_9	ν(Cl−C)
642	7.6	644.7	8.2		653.7 (10)	ν_{10}	δ(O−O−N)
510	2.4	511.4	2.0	520 m	511.6 (3.5)	ν_{11}	ν(N−O)
467	1.3	467.7	2.3	474 vs	466.2 (2.2)	ν_{12}	δ(Cl−C=O)
				359 m	356.2 (1.7)	ν_{13}	
				330 s	321.2 (1.4)	ν_{14}	
				284 s	282.8 (0.5)	ν_{15}	
				105 s	89.8 (<0.01)	ν_{16}	

^{a} Relative integrated intensities. ^{b} Most intensive matrix sites. ^{c} B3LYP/6-311+G(2df), 100% = 486 km mol^{-1}, $\nu_{17} = 80.5$ (0.03); $\nu_{18} = 70.2$ (0.1) cm^{-1}.

O−NO$_2$ bond has been determined by Kirchner et al.[24] to be 115.1 kJ mol^{-1} and by Spence et al.[23] to be 115.8 kJ mol^{-1}.

Neat ClC(O)OONO$_2$ melts at −84 °C and is a colorless liquid at room temperature. Its vapor pressure is fitted by the equation $\log(p/p°) = 4.595 - 1618.9/T$ between −60 and +10 °C. The extrapolated boiling point amounts to 80 °C, which is significantly higher than that of the fluoro analogue FC(O)OONO$_2$ (bp 32 °C).[10]

Spectroscopic Properties. (a) Vibrational Spectra. As in other acyl peroxynitrates, the ClC(O)OO moiety is expected to be nearly planar. Hence two rotamers are possible with the ClC(O) group oriented anti or syn with respect to the O−O bond:



(10)

In order to observe the individual IR spectra of these isomers, thermal effusive molecular beams of equilibrium mixtures between room temperature and 450 °C were trapped in neon matrices. However, no changes in the matrix spectra between 20 and 150 °C were recognized. At higher temperatures, the compound decomposed into NO$_2$ and ClC(O)OO radicals.[20] Therefore only one isomer exists in the temperature range 20 to 150 °C as predicted (see below). According to the quantum chemical calculations the anti form is ca. 3 kcal mol^{-1} higher in energy than the syn form and therefore the anti form should be present in equilibrium 10 by a few percent at 150 °C.

In Figure 3 the gas-phase IR and solid state (−196 °C) Raman spectra of ClC(O)OONO$_2$ are depicted. All experimental vibrational data together with a tentative assignment are listed in Table 1 and compared with wavenumbers of the fundamentals predicted by quantum chemical calculations. Due to the low symmetry (C_1) of ClC(O)OONO$_2$, all 18 fundamentals are infrared and Raman active and can be separated into 7 stretching, 8 deformation, and 3 torsional modes. In the high wavenumber range of 1850 to 900 cm^{-1} all modes are easily assignable by comparison to the spectrum of FC(O)OONO$_2$[10] and the calculated displacement vectors. The mean value of the NO$_2$ stretching modes (1545 cm^{-1}) is slightly lower than that for FC(O)OONO$_2$ (1550 cm^{-1}),[10] in accordance with the lower electronegativity of the ClC(O)OO group.[34] All further fundamentals are more or less mixed, and their description is somewhat arbitrary.

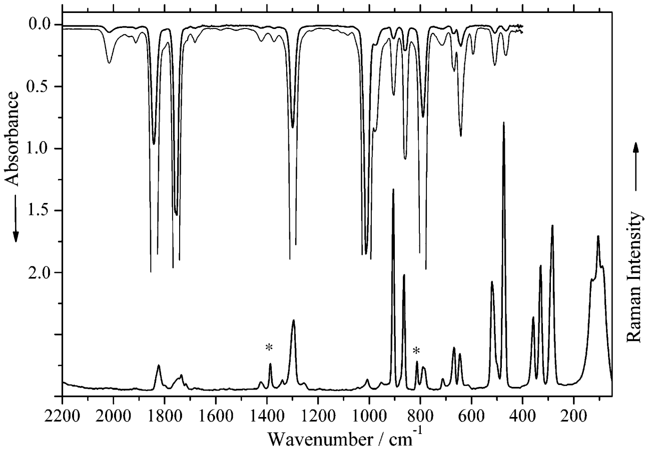


Figure 3. Gas phase IR and solid state (−196 °C) Raman spectra of ClC(O)OONO$_2$; (*) impurities.

(b) NMR Spectroscopy. The ^{13}C NMR spectrum of ClC(O)OONO$_2$ recorded at −50 °C shows a sole singlet at 148.8 ppm, which confirms the presence of a single conformer. In comparison to other acyl peroxynitrates (Table 2) there is an increment of the resonance frequency with decreasing electronegativity of the substituent, indicating that the paramagnetic term of the shielding at the carbon atom is more important than the diamagnetic term.

---

(34) Siebert, H., In *Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie*; Springer-Verlag: Berlin, 1966.

Table 2. ^{13}C Chemical Shifts for $RC(O)OONO_2$ Compounds

R	$\delta^{13}C(O)$/ppm
F[a]	144.8
Cl[b]	148.8
CF_3O[c]	145.8
CF_3[d]	155.4
CH_3[d]	167.0

[a] Reference 10. [b] This work. [c] Reference 9. [d] Reference 35.

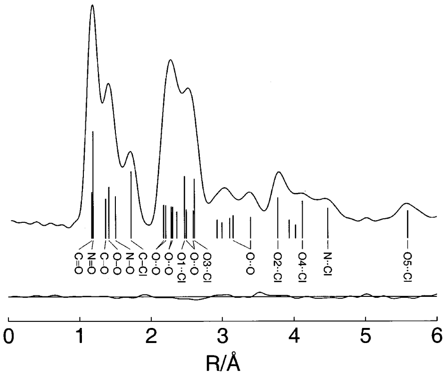


Figure 4. Experimental radial distribution function and difference curve. Important interatomic distances are indicated by vertical bars.

Table 3. Absorption Cross Section of Gaseous $ClC(O)OONO_2$

λ/nm	$10^{20}\cdot\sigma/cm^2$	λ/nm	$10^{20}\cdot\sigma/cm^2$
200	286	250	13
205	202	255	10
210	135	260	7.3
215	91	265	5.3
220	64	270	3.8
225	48	275	2.6
230	37	280	1.8
235	29	290	0.84
240	24	300	0.47
245	17		

There is not a simple correlation between the ^{13}C NMR shifts and the thermal lifetimes as suggested for other peroxynitrates.[24]

(c) UV Spectrum. In the UV region, gaseous $ClC(O)OONO_2$ shows an unstructured absorption that begins at around 300 nm and increases toward 190 nm. The absorption cross sections were obtained from several spectra of different sample pressures and are listed in Table 3. The UV spectrum is very similar in shape to the spectrum of $FC(O)OONO_2$[10] but more intensive below 240 nm. The absorption may be assigned to the $n \rightarrow \pi^*$ transition of the ClCO or NO_2 chromophores.

(d) Structure Analysis. The experimental radial distribution function (RDF), which was derived by Fourier transformation of the molecular intensities, is shown in Figure 4. This RDF can be reproduced only with a structure possessing syn orientation of the C=O bond with respect to the O–O bond. A preliminary molecular model derived from the RDF was refined by least-squares fitting of the experimental intensities. The following assumptions, based on the quantum chemical calculations (B3LYP), were made in the least squares analyses. (1) The ClC(O)O and ONO_2 moieties were constrained to planarity. (2) The two N=O bond lengths were set equal. (3) The differences between N=O and C=O bond lengths, the differences between the two O–N=O angles, and the torsional angles of the NO_2 group around the O–N bond (ϕ(O1–O2–N=O4)) and of the C(O)Cl group around the O–C bond (ϕ(O2–O1–C=O3)) were set to calculated values. Simultaneous refinement of the closely spaced N=O and C=O bond lengths resulted in high correlation and very large error limits. (4) Vibrational amplitudes were collected in groups according to the calculated values, and amplitudes which are poorly determined in the GED experiment were not refined. With these assumptions eleven geometric parameters (*p*1 to *p*11) and seven vibrational amplitudes (*l*1 to *l*7) were refined simultaneously. The following correlation coefficients had absolute values larger than 0.7: $p5/p8 = 0.72$, $p6/p9 = -0.71$, $p8/p9 = -0.74$, and $p6/p11 = -0.75$. The final results are listed together with calculated values in Table 4 (geometric parameters) and Table 5 (vibrational amplitudes).

Table 4. Experimental and Calculated Geometric Parameters for $ClC(O)OONO_2$

	GED[a]		B3LYP/ 6-311+G(2df)	MP2/ 6-311+G(2df)
C=O	1.177(2)	*p*1	1.175	1.184
N=O	1.185(2)[b]		1.183	1.185
C–O1	1.366(9)	*p*2	1.376	1.373
O–O	1.418(6)	*p*3	1.408	1.408
N–O	1.511(8)	*p*4	1.532	1.570
C–Cl	1.725(3)	*p*5	1.747	1.729
O1–O2–N	108.0(12)	*p*6	109.5	107.5
O2–O1–C	110.4(10)	*p*7	110.6	109.3
O1–C=O3	128.0(11)	*p*8	127.6	127.5
O1–C–Cl	105.7(5)	*p*9	105.6	105.6
O3=C–Cl	126.3(8)[c]		126.8	126.9
O4=N=O5	134.0(14)	*p*10	134.9	136.8
O2–N=O4	116.7(9)[d]		116.2	115.0
O2–N=O5	109.3(9)[d]		108.8	108.2
ϕ(O1–O2–N=O4)	−3.6[e]		−3.6	−1.2
ϕ(O2–O1–C=O3)	−4.6[e]		−4.6	−4.3
ϕ(C–O1–O2–N)	86.7(19)	*p*11	87.9	81.1

[a] r_{h1} values in angstroms and degrees. Error limits in parentheses are 3σ values and refer to the last digit. See Figure 1 for atom numbering. [b] Difference to previous parameter fixed to calculated (B3LYP) value. [c] Dependent parameter. [d] The difference between the two O–N=O angles was constrained to the calculated (B3LYP) values. [e] Not refined. The negative sign of the torsional angle implies shortening of the O3···O4 distance.

Considering experimental uncertainties and systematic differences between vibrationally averaged bond distances (r_{h1}) and calculated equilibrium values (r_e), the B3LYP method reproduces bond lengths, bond angles, and the dihedral angle ϕ(C–O–O–N) very well. On the other hand, the MP2 approximation predicts the N–O bond too long by about 0.06 Å and the dihedral angle too small by about 8°. Similar observations have been made previously for $CH_3C(O)OONO_2$ and $CF_3C(O)OONO_2$. For both peroxynitrates the DFT method (B3LYP) reproduces the experimental structures satisfactorily, whereas the MP2/6-31G* approximation predicts O–N bond lengths too long by about 0.05 to 0.06 Å and the dihedral angles too small by about 5°. This failure of the MP2 approximation in predicting O–N bond distances is independent of the size of the basis set.

Table 6 compares relevant skeletal geometric parameters of peroxynitrates $ROONO_2$, whose structures have been determined in the gas phase. The mean O–O bond length, 1.416 ± 0.019 Å, is shorter than that in peroxides with

Table 5. Interatomic Distances, Vibrational Amplitudes, and Corrections

	distance	ampl (GED)[a]		ampl (B3LYP)[b]	$\Delta r = r_{h1} - r_a$
C═O	1.18	0.037(2)	*l*1	0.036	0.0011
N═O	1.19	0.037(2)	*l*1	0.037	0.0012
C−O	1.37	0.049(4)	*l*2	0.049	0.0018
O−O	1.41	0.049(4)	*l*2	0.049	0.0017
N−O	1.51	0.065[c]		0.065	0.0028
C−Cl	1.72	0.049(4)	*l*2	0.050	0.0015
O4···O5	2.18	0.045[c]		0.045	0.0037
O2···O5	2.21	0.067[c]		0.067	0.0049
O2···C	2.27	0.065(5)	*l*3	0.063	0.0030
O1···O3	2.29	0.054(5)	*l*4	0.052	0.0042
O2···O4	2.30	0.065(5)	*l*3	0.064	0.0045
O1···N	2.36	0.070[c]		0.070	0.0032
O1···Cl	2.47	0.065(5)	*l*3	0.064	0.0052
O1···O4	2.50	0.097[c]		0.097	−0.0033
O2···O3	2.60	0.092[c]		0.092	−0.0001
Cl···O3	2.60	0.054(5)	*l*4	0.057	0.0045
C···O4	2.93	0.187[c]		0.187	0.0058
C···N	3.00	0.126(12)	*l*5	0.127	0.0078
N···O3	3.10	0.193(35)	*l*6	0.212	0.0130
O3···O4	3.15	0.257(82)	*l*7	0.283	0.0254
O1···O5	3.39	0.065(5)	*l*3	0.064	0.0129
O2···Cl	3.78	0.065(5)	*l*3	0.064	0.0138
O3···O5	3.93	0.257(82)	*l* 7	0.248	0.0202
C···O5	4.02	0.126(12)	*l*5	0.136	0.0183
Cl···O4	4.12	0.193(35)	*l*6	0.225	0.0113
Cl···N	4.48	0.126(12)	*l*5	0.133	0.0197
Cl···O5	5.59	0.126(12)	*l*5	0.119	0.0357

[a] Values in angstroms; error limits are 3σ values and refer to the last digit. For atom numbering see Figure 1. [b] 6-31G* basis sets. [c] Not refined.

electropositive substituents (1.464 Å in HOOH,[35] 1.457(12) Å in MeOOMe[36]). On the other hand, the mean N−O bond, 1.513 ± 0.018 Å, is much longer than that in covalent nitrates with electropositive substituents (1.406(5) Å in $HONO_2$,[37] 1.402(5) Å in $MeONO_2$ [38]). This mean N−O bond length is even larger than that in $FONO_2$ (1.507(4) Å[39]) and correlates with the easy dissociation of $ClC(O)OONO_2$ into ClC(O)OO and NO_2 radicals. The mean dihedral angle (ϕ(COON) = 86 ± 2°) in peroxynitrates with R = C(O)X is smaller than 90°.

Table 6. Important Skeletal Parameters of Peroxynitrates, $ROONO_2$ (Å and deg)

$ROONO_2$	O−O	N−O	ϕ(C−O −O−N)
CF_3OONO_2[a]	1.414(8)	1.523(7)	108.1(16)
$CH_3C(O)OONO_2$[b]	1.418(12)	1.492(7)	84.7(13)
$CF_3C(O)OONO_2$[b]	1.408(8)	1.526(10)	85.8(29)
$FC(O)OONO_2$[c]	1.420(6)	1.514(6)	86.2(14)
$ClC(O)OONO_2$[d]	1.418(6)	1.511(8)	86.7(19)

[a] Reference 5. [b] Reference 8. [c] Reference 10. [d] This work.

In the gas electron diffraction experiment, only the syn conformer of $ClC(O)OONO_2$ is observed. This result is in agreement with the interpretation of the matrix IR spectra which demonstrated the presence of a single conformer only, even at 150 °C. If we assume that an upper limit of 5% of the anti form could exist and remained undetected at this temperature, we obtain $\Delta G^\circ = G^\circ_{(anti)} - G^\circ_{(syn)} > 2.8$ kcal mol^{-1}.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and Volkswagen Stiftung are gratefully acknowledged.

IC050229L

---

(35) Koput, J. *J. Mol. Spectrosc.* **1986**, *115*, 438−441.
(36) Haas, B.; Oberhammer, H. *J. Am. Chem. Soc.* **1984**, *106*, 6146−6149.
(37) Cox, A. P.; Riveros, J. M. *J. Chem. Phys.* **1965**, *42*, 3106−3112.
(38) Cox, A. P.; Waring, S. *Trans. Faraday Soc.* **1971**, *67*, 3441−3450.
(39) Casper, B.; Dixon, D. A.; Mack, H. G.; Ulic, S.; Willner, H.; Oberhammer, H. *J. Am. Chem. Soc.* **1994**, *116*, 8317−8321.