Thermochimica Acta, 216 (1993) 81–85
Elsevier Science Publishers B.V., Amsterdam

On the thermodynamics of the ClOO and OClO radicals [1]

Zdeněk Slanina [2] and Filip Uhlík [3]

Max-Planck-Institut für Chemie (Otto-Hahn-Institut), D-W-65 Mainz (Germany)

(Received 10 June 1992)

Abstract

The thermodynamics of the isomeric radicals ClOO and OClO is treated on the basis of ab initio computed parameters. Regardless of the source of the inter-isomeric energetics, the ClOO species is predominant although the other structure can also become significant at higher temperatures. The presence of the less stable species increases the molar heat capacity by no more than about 5%. The results are of importance for ozone-depletion mechanisms.

INTRODUCTION

Chlorine oxides represent the most important agents studied in connection with (Antarctic) ozone depleting mechanisms [2–8]. Examples are the ClO and Cl_2O_2 species [9–11] and the ClOO and OClO radicals [12–19]. Recent computations in our laboratory [20] provided ab initio structural, energetic, and vibrational parameters for the two last-mentioned radicals. A uniform data set allows a deeper investigation of the relative stabilities of these two isomeric species, and this is the subject of the present study.

COMPUTATIONS

The computations [20] were carried out with the GAUSSIAN 88 program system [21] in the standard 6-31G* basis set combined with an electron-correlation evaluation by the second-order Møller–Plesset (MP2) perturbation treatment considering all electrons. Within the MP2/6-31G*

Correspondence to: Z. Slanina, Limburgs Universitair Centrum, Departement SBG, Universitaire Campus, Gebouw D, B-3590 Diepenbeek, Belgium.

[1] Part IV in the series "Computational Studies of Atmospheric Chemistry Species"; for Part III, see ref. 1.

[2] On a leave of absence from the Czechoslovak Academy of Sciences, Prague.

[3] Permanent address: Faculty of Science, Charles University, Prague, Czech Republic.

TABLE 1

Relative[a] energies ΔE of the ClOO and OClO isomers

Approach	ΔE (kJ mol^{-1})	
	ClOO	OClO
MP2/6-31G*[b]	0.0	16.18
MP4/6-31G*[b]	0.0	42.35

[a] Relative to the ClOO species. [b] The energetics evaluated [9] in the MP2/6-31G* optimum geometry.

approach geometry optimization and harmonic vibrational analysis were performed. Moreover, in the MP2/6-31G* energy minima the full fourth-order Møller–Plesset (MP4) correlation energy calculations were carried out. Two minimum-energy structures (ClOO and OClO) were found; Table 1 surveys their energetics. The ClOO structure is more stable in both the MP2/6-31G* and MP4/6-31G* approaches. Although the MP4/6-31G* treatment is more sophisticated, we shall (for methodological reasons) investigate the inter-isomeric thermodynamics in both energetics.

In an n-membered equilibrium isomeric set at non-zero temperature, all its members are present, although their relative populations are temperature dependent. Let the mole fraction of the ith component of the isomeric equilibrium mixture be w_i. In terms of the ground state energy $\Delta H^{\ominus}_{0,i}$ (i.e. the standard enthalpy at temperature 0 K) and the isomeric partition function q_i, the mole fraction is given by [22–24]

$$w_i = \frac{q_i \exp[-\Delta H^{\ominus}_{0,i}/(RT)]}{\sum_{j=1}^{n} q_j \exp[-\Delta H^{\ominus}_{0,j}/(RT)]} \tag{1}$$

where R stands for the gas constant and T for the temperature. The partition function q_i is determined in this study by using the computed parameters [20] under the rigid-rotor harmonic-oscillator [23] approximation.

Once we deal with an equilibrium isomeric mixture, two classes of molar thermodynamic terms can be distinguished: overall many-component thermodynamic terms $\Delta X^{\ominus}_T$ and partial one-component terms $\Delta X^{\ominus}_i$. It is convenient to study isomerism effects by means of the so-called isomerism contributions [24] to thermodynamic terms δX_1, i.e.

$$\delta X_1 = \Delta X^{\ominus}_T - \Delta X^{\ominus}_1 \tag{2}$$

The most stable species (in the low temperature limit) is usually chosen as the reference structure and labelled by $i = 1$ (i.e. the ClOO structure in our particular case). The heat capacity at constant pressure $X = C_p$ represents an especially interesting term, owing to temperature maxima induced by the isomeric interplay (for the underlying formulae for the isomerism contribution to the heat capacity $\delta C_{p,1}$, see ref. 24).

RESULTS AND DISCUSSION

Although the ClOO and OClO radicals are quite small systems they still exhibit significant differences. They differ in their symmetry numbers (1 and 2 for the ClOO and OClO isomers, respectively) and in the products of the moments of inertia. Further, the calculated MP2/6-31G* harmonic vibrational frequencies [20] of the ClOO isomer (498, 1095, 1717 cm^{-1}) are systematically higher than the corresponding values for the other species (424, 987, 1116 cm^{-1}). Hence, this allows for differences in entropy.

This study can present for the first time the relative populations of the two radicals (Table 2) under the conditions of the interisomer thermodynamic equilibrium. In the low temperature region the ClOO species essentially predominates. However, with a temperature increase the other species also becomes significant. Their relative stabilities are considerably sensitive to the potential energy term. In the MP2/6-31G* energetics a high-temperature limit for the ClOO/OClO ratio is about 2:1, whereas in the MP4/6-31G* energetics it approaches a value close to 6:1.

Table 3 deals with the enhancement of the heat capacity term by the isomeric interplay. The isomerism contribution to the heat capacity $\delta C_{p,1}$ exhibits a temperature course with a maximum in both energetics considered. Although the magnitude of the maximum is quite similar, its temperature position differs considerably. In fact, the maximum is located close to a region of relatively fast temperature changes in the relative stabilities and those are quite sensitive to the energetics. However, the temperature maxima are not apparent in the overall molar heat capacity term C_p°, owing to the fact that they are overlapped by temperature increase of the latter term itself. However, we can still observe a temperature

TABLE 2

Equilibrium mole fractions w_i for the ClOO and OClO species in the MP2/6-31G* and MP4/6-31G* energetics at selected temperatures

T (K)	MP2/6-31G*		MP4/6-31G*	
	w_{ClOO} (%)	w_{OClO} (%)	w_{ClOO} (%)	w_{OClO} (%)
298.15	99.6	0.4	100.0	1×10^{-5}
500	97.1	3.0	100.0	6×10^{-3}
1000	87.5	12.5	99.4	0.6
2000	74.8	25.2	93.5	6.5
3000	68.8	31.2	86.3	13.7

TABLE 3

Specification of temperature maxima[a] in heat capacity enhancement by temperature interplay of the ClOO and OClO isomers

Type[a]	Approach	T (K)	w_{ClOO} (%)	$\delta C_{p,1}$[b] (J K^{-1} mol^{-1})	C_p° (J K^{-1} mol^{-1})	$\frac{\delta C_{p,1}}{C_p^\circ}$ (%)
$\delta C_{p,1}$ maximum	MP2/6-31G*	806	91.1	2.83	54.0	5.24
	MP4/6-31G*	2157	92.3	3.14	60.1	5.23
$\frac{\delta C_{p,1}}{C_p^\circ}$ maximum	MP2/6-31G*	729	92.7	2.80	52.9	5.29
	MP4/6-31G*	2122	92.6	3.14	60.0	5.23

[a] Maximum in the isomerism contribution[b] to heat capacity $\delta C_{p,1}$, or maximum in the relative enhancement $\delta C_{p,1}/C_p^\circ$ of the overall C_p°. [b] Isomerism contribution to heat capacity is related to the more-stable species, i.e. to the ClOO isomer.

maximum in the relative enhancement of the overall term, i.e. in the quotient $\delta C_{p,1}/C_p^\circ$. The temperature maximum in the quotient is located somewhat below the temperature of the $\delta C_{p,1}$ maximum. Interestingly enough, the height of the $\delta C_{p,1}/C_p^\circ$ maximum is practically independent of the energetics applied. Hence, we can conclude that the overall heat capacity term is enhanced by the equilibrium isomeric interplay by about 5.3% at most. Generally speaking, such an increase could have, for some atmospheric species, significant consequences for atmospheric thermophysics.

ACKNOWLEDGEMENT

Part of this study was carried out during a research stay by Z.S. at the Max-Planck-Institut für Chemie (Otto-Hahn-Institut), supported both by the Institute and the Alexander von Humboldt-Stiftung. The support of and the valuable discussions with Professors Paul J. Crutzen and Karl Heinzinger are gratefully acknowledged.

REFERENCES

1 Z. Slanina and L. Adamowicz, J. Atmos. Chem., in press.
2 S. Solomon, R.R. Garcia, F.S. Rowland and D.J. Wuebbles, Nature, 321 (1986) 755.
3 P.J. Crutzen and F. Arnold, Nature, 324 (1986) 651.
4 L.T. Molina and M.J. Molina, J. Phys. Chem., 91 (1987) 433.
5 M.J. Molina, T.L. Tso, L.T. Molina and F.C.Y. Wang, Science, 238 (1987) 1253.
6 D.W. Toohey and J.G. Anderson, J. Phys. Chem., 92 (1988) 1705.
7 S.B. Moore, L.F. Keyser, M.-T. Leu, R.P. Turco and R.H. Smith, Nature, 345 (1990) 333.
8 Th. Peter, C. Brühl and P.J. Crutzen, Geophys. Res. Lett., 18 (1991) 1465.
9 M.P. McGrath, K.C. Clemitshaw, F.S. Rowland and W.J. Hehre, J. Phys. Chem., 94 (1990) 6126.
10 Z. Slanina and F. Uhlík, J. Phys. Chem., 95 (1991) 5432.

11 Z. Slanina and F. Uhlík, Int. J. Thermophys., 13 (1992) 303.
12 J.B. Coon and E. Ortiz, J. Mol. Spectrosc., 1 (1957) 81.
13 A. Arkell and I. Schwager, J. Am. Chem. Soc., 89 (1967) 5999.
14 H.S. Johnston, E.D. Morris, Jr. and J. van den Bogaerde, J. Am. Chem. Soc., 91 (1969) 7712.
15 A. Hinchliffe, J. Mol. Struct., 64 (1980) 117.
16 J.A. Jafri, B.H. Lengsfield III, C.W. Bauschlicher, Jr. and J.H. Phillips, J. Chem. Phys., 83 (1985) 1693.
17 K. Miyazaki, M. Tanoura, K. Tanaka and T. Tanaka, J. Mol. Spectrosc., 116 (1986) 435.
18 J.M. Nicovich, K.D. Kreutter, C.J. Shackelford and P.H. Wine, Chem. Phys. Lett., 179 (1991) 367.
19 R.L. Mauldin III, J.B. Burkholder and A.R. Ravishankara, J. Phys. Chem., 96 (1992) 2582.
20 Z. Slanina, F. Uhlík and R. Ponec, Struct. Chem., to be published.
21 M.J. Frisch, M. Head-Gordon, H.B. Schlegel, K. Raghavachari, J.S. Binkley, C. Gonzalez, D.J. DeFrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R. Martin, L.R. Kahn, J.J.P. Stewart, E.M. Fluder, S. Topiol, J.A. Pople, GAUSSIAN 88, Gaussian Inc., Pittsburgh, PA, 1988.
22 Z. Slanina, Adv. Quantum Chem., 13 (1981) 89.
23 Z. Slanina, Contemporary Theory of Chemical Isomerism, Academia and Reidel, Prague and Dordrecht, 1986.
24 Z. Slanina, Int. Rev. Phys. Chem., 6 (1987) 251.