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Dimerization equilibrium constant for the ClO radical. State-of-the-art wide-temperature-interval thermodynamics of species related to ozone depleting [a]

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Abstract

The recently computed energetics and molecular parameters of the components of the $ClO/Cl_2O_2(g)$ system are employed in evaluation of the ClO radical dimerization thermodynamics. The computed data have been partly refined in order to reproduce observed dimerization equilibrium constants. An analytical extrapolation formula is suggested, representing the best contemporary tool for the equilibrium constant K_p estimation $\log_{10}K_p = -3.644 - 1142/T^2 + 3704/T - 1.580 \log_{10}T + 1.048 \times 10^{-3}T - 1.058 \times 10^{-7}T^2$, with K_p in atm^{-1} and temperature T in Kelvin. The formula has been constructed for a wide temperature interval between 50 and 1000 K. Within the treatment, the computationally predicted isomerism (ClOOCl, $ClClO_2$, or ClOClO structure) is considered accordingly. The recommended extrapolation formula represents an input information for further applications, especially in ozone-depletion mechanism elucidation.

INTRODUCTION

The gas-phase dimerization of the ClO radical has been studied quite recently [1–5] by computational means which supplied useful information not obtainable from the available observations of the ClO/Cl_2O_2 system [6–18]. Experimental data [13,18] on thermodynamics of the radical dimerization

$$2ClO(g) = Cl_2O_2(g) \tag{1}$$

are available for a rather narrow temperature interval so that an extrapolation for temperatures outside the interval would be connected with some

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uncertainty. Extrapolation for still lower temperatures is particularly interesting with respect to the supposed role of the system (1) in ozone-depletion mechanisms [19–21]. Data at higher temperatures can generally be of use in radical chemistry.

Computational studies [1–5] revealed one interesting feature of the Cl_2O_2 species, namely its isomerism. Three local minima (all of them non-planar and singlet electronic states) were found [1,3] on the potential energy hypersurface. Chlorine peroxide ClOOCl (C_2 point group of symmetry) was found to be the lowest in potential energy, followed by hypervalent chloryl chloride $ClClO_2$ (C_s symmetry) and finally by unsymmetrical (C_1) hypervalent chlorine chlorite ClOClO. The thermodynamic consequences of the isomerism have already been considered [5] (using the calculated energetics [3,5]) and interesting effects were found. Meanwhile, a third source of the system energetics has been published [4]. The present study compares all three computational energetics [3–5] and recommends the current best evaluation of the equilibrium constant of reaction (1) (in a form of analytical function of temperature). In addition, isomerism effects are studied within the newest energetics [4].

COMPUTATIONS

The equilibrium constant

$$K_p = \frac{p_{Cl_2O_2}}{p^2_{ClO}} \tag{2}$$

represents a key quantity in our computations. It can be calculated [22] in terms of partition functions and energetics. With respect to the available extent of information, the partition functions are to be of the rigid-rotor and harmonic-oscillator (RRHO) quality. If we accept the computational fact [1–5] of Cl_2O_2 isomerism and impose thermodynamic equilibrium between the isomers, i.e. considering the dimer as one complex pseudospecies, the equilibrium constant K_p becomes a quantity of composed, overall nature. The overall equilibrium constant K_p is however simply related to the partial (one isomer) equilibrium constants $K_{p,i}$

$$K_p = \sum_{i=1}^{3} K_{p,i} \tag{3}$$

where i stands for the C_2, C_s or C_1 isomer.

In the present study, three sets of dimerization and isomerization energetics are employed; Table 1 gives the dimerization ground-state energy changes $\Delta H^{\ominus}_{0,i}$ for the C_2 and C_s isomers. Two sets originated from ab initio calculations and are coded in this report by MCRH [1,3] and SRBT [4]. The third energy set was derived [5] from a generalization of so-called

TABLE 1

Survey of the considered calculated ClO dimerization energetics [a] for ClOOCl and ClClO$_2$ isomers [b]

Approach	Source	$\Delta H_{0,1}^{\ominus}$ [a] (kJ mol^{-1})	$\Delta H_{0,2}^{\ominus}$ [a] (kJ mol^{-1})	Acronym
Ab initio	[3]	−66.20	−61.18	MCRH
Ab initio	[4]	−79.27	−46.83	SRBT
Fitting	[5]	−69.53	−66.64	RTln/9

[a] Ground-state energy changes, i.e. enthalpy changes at the absolute zero temperature, $\Delta H_{0,i}^{\ominus}$ for dimerization to ClOOCl (C_2 symmetry, $\Delta H_{0,1}^{\ominus}$) or ClClO$_2$ (C_s symmetry, $\Delta H_{0,2}^{\ominus}$).
[b] The third isomer (ClOClO with C_1 symmetry) is always located in the ground-state energy scale about 31 kJ mol^{-1} above the C_2 one (as suggested in refs. 1 and 3).

third-law analysis combining the nine observed K_p values [18] with the thermodynamic-potential changes calculated from molecular parameters [3,11,12] in order to best reproduce the Gibbs energy changes. This fitting procedure is coded here by RTln/9. For simplicity, the energy of the third isomer (C_1 symmetry) was described in a unified way in all three sets, namely as being higher in ground-state energy than the C_2 structure by about 31 kJ mol^{-1} (as found by MCRH [3]).

The overall equilibrium constant K_p for each of the three energy sets was calculated within a wide temperature interval from 50 to 1000 K and the values were fitted to the following six-term analytical form

$$\log_{10} K_p = A + \frac{B}{T^2} + \frac{C}{T} + D \log_{10} T + ET + FT^2 \tag{4}$$

The interplay of the three isomeric forms of the dimer can be studied still more comprehensively than suggested by eqn. (3). Mole fractions w_i of the three isomers in their equilibrium mixture are related to the partition functions q_i and energetics as follows [22–24]

$$w_i = \frac{q_i \exp\left[-\Delta H_{0,i}^{\ominus}/(RT)\right]}{\sum_{j=1}^{3} q_j \exp\left[-\Delta H_{0,j}^{\ominus}/(RT)\right]} \tag{5}$$

In analogy to the equilibrium constants, the partial and overall quantities can be considered for any thermodynamic term, X. The standard partial terms $\Delta X_i^{\ominus}$ belong to processes dealing with the individual isomers, the overall terms $\Delta X_T^{\ominus}$ to processes in which the equilibrium isomeric mixture acts as one pseudo-species. In addition to the partial and overall terms a third quantity has been introduced [22–24], the so-called isomerism contributions to thermodynamic terms δX_1, related to the reference structure 1, defined as

$$\delta X_1 = \Delta X_T^{\ominus} - \Delta X_1^{\ominus} \tag{6}$$

TABLE 2

Expansion coefficients in the six-term analytical form [a] for temperature dependence of the ClO(g) dimerization equilibrium constant K_p [b]

Energetics	A	B	C	D	E	F
MCRH	-2.291	-1407	3524	-2.278	2.131×10^{-3}	-4.968×10^{-7}
SRBT	0.2515	-185.7	4140	-3.274	2.141×10^{-3}	-2.210×10^{-7}
RTln/9	-3.644	-1142	3704	-1.580	1.048×10^{-3}	-1.058×10^{-7}

[a] $\log_{10}K_p = A + B/T^2 + C/T + D\log_{10}T + ET + FT^2$.

[b] The related standard-state choice – an ideal gas at 1 atm = 101325 Pa pressure; K_p in atm^{-1}, T in K.

Specific formulae for enthalpy ($X = H$), entropy ($X = S$) and heat capacity at constant pressure ($X = C_p$) are given elsewhere [22–24].

RESULTS AND DISCUSSION

Table 2 presents the expansion coefficients for the analytical form given in eqn. (4) for the three considered energy sets. It has already been pointed out [5] that the ab initio MCRH energetics produces a systematic underestimation with respect to the observed data [13,18]. The newer ab initio SRBT data [4], in contrast, lead to systematic overestimation. The third energetics, the RTln/9 fitting, produces a fairly smooth interpolation through the observed values [13,18] which is in agreement with the nature of the fitting treatment used [5]. Figure 1 documents the behaviour within

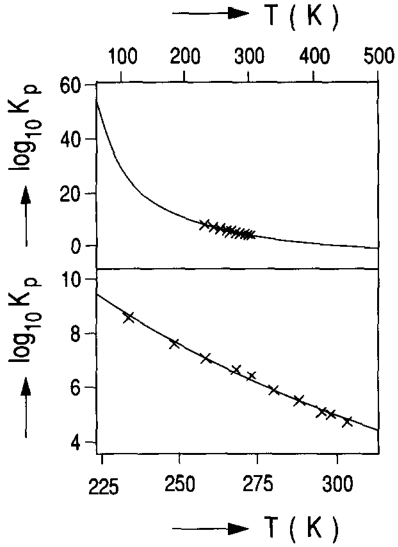

Fig. 1. Observed values [13,18] of the ClO(g) dimerization equilibrium constant (×) and the RTln/9 calculated dependency depicted in two temperature intervals.

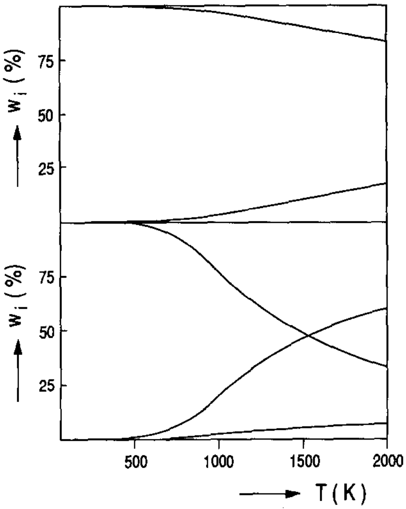

Fig. 2. Temperature dependences of the weight factors w_i for Cl_2O_2 isomers evaluated in SRBT energetics; the upper and lower parts refer to the two- and three-membered isomeric mixtures, respectively. The order of the w_i terms at 1000 K is (from the highest to the lowest) C_2, C_s (the upper part) and C_2, C_1, C_s (the lower part).

two temperature intervals. Naturally, the last mentioned energetics represents the best tool for further extrapolation and thus, the analytical expression with the RTln/9 expansion coefficients is highly recommended for any further use. Interestingly enough, the RRHO approximation of partition functions is not critical in conjunction with the RTln/9 energetics as an inter-compensation mechanism operates within the fitting applied.

The newer SRBT *ab initio* energetics [4] was never tested for isomeric interplay effects. Hence, this report ends with such a study, even though it is not important for our primary aim — the resulting K_p extrapolation formula deals with the RTln/9, not the SRBT, energetics. However, in the SRBT energetics (Table 1) the two higher isomers are very close in energy, this being quite an interesting situation from the methodical point of view. In fact, in the applied conjunction with the MCRH C_1 separation energy, the latter species is even more stable in the ground-state energy than the C_s one, by about 1.5 kJ mol^{-1}. Figure 2 presents the temperature dependences of the weight factors w_i for two-membered (C_2 and C_s) and three-membered (C_2, C_s and C_1) isomeric sets. It is clearly evident that the C_1 species becomes important at high temperatures, in contrast to the C_s structure which is otherwise close in energy. The C_1 structure finally exhibits even higher relative stability than the deepest C_2 minimum. However, temperatures relevant for the stability interchange are too high from a practical point of view.

Figure 3 shows the temperature evolution of the isomerism contributions (eqn. (6)) to the enthalpy, entropy and heat capacity terms. Again, compari-

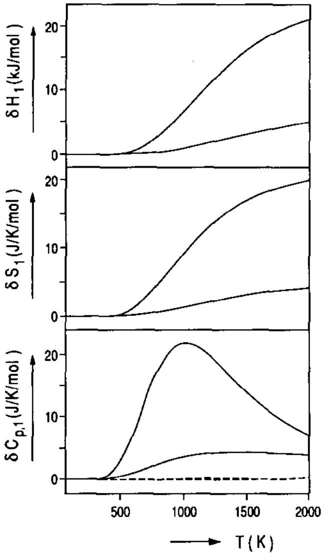

Fig. 3. Temperature dependences of the isomerism contributions to enthalpy δH_1, entropy δS_1 and heat capacity at constant pressure $\delta C_{p,1}$ (relaxation [23,24] term) or $\delta C_{p,w,1}$ (isofractional [23,24] term, broken lines) for the Cl_2O_2 isomeric system evaluated in the SRBT energetics; the contributions are related to the C_2 species as the reference structure. In each related pair of curves the higher and lower refer to the three- and two-membered isomeric mixture, respectively (compare Fig. 2).

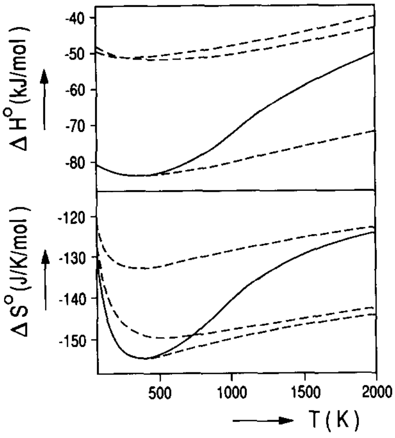

Fig. 4. The upper part: temperature dependences of the partial (broken lines) and overall standard enthalpy changes for ClO(g) dimerization evaluated in the SRBT energetics (the partial-term order at 1000 K is C_1 (highest), C_s and C_2 (lowest)). The lower part: temperature dependences of the partial (broken lines) and overall standard entropy changes for ClO(g) dimerization evaluated in the SRBT energetics (the partial-term order at 1000 K is C_1 (highest), C_s and C_2 (lowest)).

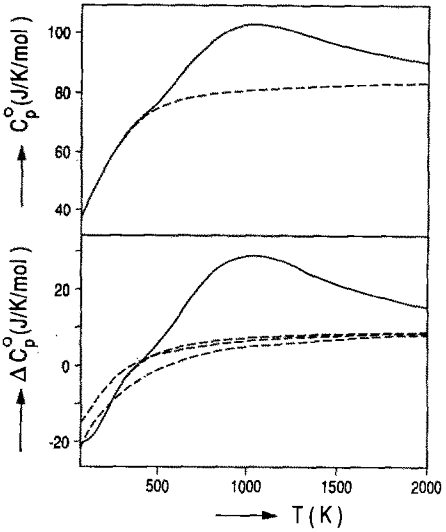

Fig. 5. The upper part: temperature dependences of the standard molar heat capacity at constant pressure for the pure C_2 isomer (broken line, the partial $C_{p,1}^{\ominus}$ term) and for the equilibrium mixture of the three isomers of Cl_2O_2 (solid line, the overall $C_p^{\ominus}$ term) evaluated in the SRBT energetics. The lower part: temperature dependences of the partial (broken lines) and overall standard changes in heat capacity at constant pressure for ClO(g) dimerization evaluated in the SRBT energetics (the partial-term order at 1000 K is C_2 (highest), C_1 and C_s (lowest)).

son is made for the two-membered (C_2 and C_s) and three-membered (C_2, C_s and C_1) isomeric sets, providing further evidence of the importance of the C_1 species at high temperatures. There is an interesting feature in the

TABLE 3

Characterization of some distinguished [a] points of the Cl_2O_2 isomeric interplay within the SRBT energetics

Type [a]	T (K)	w_1 [b] (%)	w_2 [b] (%)	w_3 [b] (%)	$\delta C_{p,1}$ [c] (J K^{-1} mol^{-1})	$C_p^{\ominus}$ (J K^{-1} mol^{-1})	$\delta C_{p,1}/C_p^{\ominus}$ (%)
Cross	1530	47.2	5.6	47.2	12.8	94.9	13.5
M:$\delta C_{p,1}$	1007	76.7	2.7	20.5	21.7	102	21.2
M:$C_p^{\ominus}$	1036	74.8	2.9	22.3	21.7	103	21.1
M:%	1000	77.3	2.7	20.1	21.7	102	21.2

[a] Cross, point of two-isomer equimolarity; M:$\delta C_{p,1}$ maximum in the isomerism contribution to heat capacity $\delta C_{p,1}$; M:$C_p^{\ominus}$ maximum in the standard overall heat capacity at constant pressure $C_p^{\ominus}$; M:% maximum of the relative enhancement $\delta C_{p,1}/C_p^{\ominus}$ of the $C_p^{\ominus}$ term by isomeric interplay.

[b] The mole fraction of the species in the equilibrium isomeric mixture; 1, 2, and 3 denote the C_2, C_s and C_1 isomers, respectively.

[c] Isomerism contribution to heat capacity related to the species most stable in the very low temperature region, i.e. to the C_2 isomer.

case of the heat capacity contribution — a temperature maximum, already reported with several other systems [23,24]. The isomerism contributions cannot be measured directly and therefore Figs. 4 and 5 show the partial and overall standard enthalpy, entropy and heat capacity at constant pressure changes. Figure 5 also compares the C_2 partial and overall Cl_2O_2 standard molar heat capacity. The temperature maximum observed with the isomerism contribution to heat capacity is conserved in both overall heat capacity terms.

Finally, Table 3 gives a detailed specification of some important points of the temperature dependences reported in Figs. 2, 3 and 5. The magnitude of the isomerism effects represents a further interesting particular illustration of general phenomena [22–24].

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REFERENCES

1 M.P. McGrath, K.C. Clemitshaw, F.S. Rowland and W.J. Hehre, Geophys. Res. Lett., 15 (1988) 883.
2 F. Jensen and J. Oddershede, J. Phys. Chem., 94 (1990) 2235.
3 M.P. McGrath, K.C. Clemitshaw, F.S. Rowland and W.J. Hehre, J. Phys. Chem., 94 (1990) 6126.
4 J.F. Stanton, C.M.L. Rittby, R.J. Bartlett and D.W. Toohey, J. Phys. Chem., 94 (1990) 6126.
5 Z. Slanina and F. Uhlík, Chem. Phys. Lett., (1991), 182 (1991) 51.
6 D.R. Stull (Ed.), JANAF Thermochemical Tables, Dow Chemical Company, Midland, 1965.
7 M.M. Rochkind and G.C. Pimentel, J. Chem. Phys., 46 (1967) 4481.
8 W.G. Alcock and G.C. Pimentel, J. Chem. Phys., 48 (1968) 2373.
9 L. Andrews and J.I. Raymond, J. Chem. Phys., 55 (1971) 3087.
10 F.K. Chi and L. Andrews, J. Phys. Chem., 77 (1973) 3062.
11 N. Basco and R.D. Morse, J. Mol. Spectrosc., 45 (1973) 34.
12 J.A. Coxon, W.E. Jones and E.G. Skolnik, Can. J. Phys., 54 (1976) 1043.
13 N. Basco and J.E. Hunt, Int. J. Chem. Kinet., 11 (1979) 649.
14 S.C. Bhatia and J.H. Hall, Jr., Inorg. Chem., 20 (1981) 629.
15 R.C. Loupec and J. Potier, J. Chim. Phys., 80 (1983) 449.
16 L.T. Molina and M.J. Molina, J. Phys. Chem., 91 (1987) 433.
17 M.J. Molina, T.L. Tso, L.T. Molina and F.C.Y. Wang, Science, 238 (1987) 1253.
18 R.A. Cox and G.D. Hayman, Nature, 332 (1988) 796.
19 P. Crutzen and F. Arnold, Nature, 324 (1986) 651.

20 J.W. Barrett, P.M. Solomon, R.L. de Zafra, M. Jaramillo, L. Emmons and A. Parrish, Nature, 336 (1988) 455.
21 R.T. Watson, in R.R. Jones and T. Wigley (Eds.), Ozone Depletion, Health and Environmental Consequences, Wiley, Chichester, 1989.
22 Z. Slanina, Contemporary Theory of Chemical Isomerism, Academia and Reidel, Prague and Dordrecht, 1986.
23 Z. Slanina, Int. Rev. Phys. Chem., 6 (1987) 251.
24 Z. Slanina, J. Phys. Chem., 92 (1988) 5836.