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A Refined Evaluation of the Gas-Phase Dimerization Thermodynamics of the ClO Radical

Z. Slanina[1,2] **and F. Uhlík**[3]

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The title reaction was treated as a convolution of three partial dimerizations, *viz.*, formation of ClOOCl, $ClClO_2$, or ClOClO isomer. Energetics of the dimerizations are derived from a fit to available data in combination with recent quantum-chemical calculations. The thermodynamics of the processes is evaluated with the help of partition functions with the calculated molecular parameters, while due respect has been paid to the dimer isomerism. The isomerism can be particularly significant in evaluating the heat-capacity term, increasing it by more than 10% at some temperatures. The most reliable values of the standard thermodynamic dimerization terms are selected for further applications, especially for elucidating ozone-depletion mechanisms.

KEY WORDS: ClO(*g*) radical dimerization; generalized third-law analysis; isomeric mixtures; ozone depletion mechanisms.

1. INTRODUCTION

A generalization of the "third law analysis" for the determination of energetics from equilibrium data has been suggested [1] for isomeric mixtures and applied to diverse problems [2–4]. The generalized treatment uses calculated standard thermodynamic potentials of all reaction species involved and determines the enthalpy changes at absolute zero temperature (simultaneously for all isomers considered) from a fit to the observed

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[1] Max-Planck-Institut für Chemie (Otto-Hahn-Institut), W-6500 Mainz, Germany.

[2] Permanent address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8-Kobylisy, Czech and Slovak Federal Republic.

[3] Faculty of Science, Charles University, Prague 2, Czech and Slovak Federal Republic.

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equilibrium-constant temperature dependence. The treatment presupposes a sufficiently large and accurate equilibrium-constant input data set.

Gas-phase dimerization of the ClO radical [5, 6] has recently been the subject of considerable interest in view of its supposed role in ozone-depletion mechanisms [7–9]:

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

This can be considered as a particular system where application of the generalized third-law analysis is pertinent. Although Cl_2O_2 species have been studied experimentally [10–17], for a more complete picture a combination with quantum-chemical calculations [18–20] is still necessary and useful. The computational studies [18–20] have revealed and characterized an essential structural isomerism of the dimer. Three structures (all of them being nonplanar and singlet electronic states) were proved [18, 20] to be local potential-energy minima. Chlorine peroxide ClOOCl (C_2 point group of symmetry) was found to be the lowest species in the ground-state energy scale (i.e., the zero-temperature enthalpy scale). The second isomer, hypervalent chloryl chloride, $ClClO_2$ (C_s symmetry), lies in the scale quite close to the peroxide structure. The third species, unsymmetrical (C_1) hypervalent chlorine chlorite, ClOClO, is higher in the energy by more than 30 kJ · mol^{-1}. In view of the computational findings, the reaction expressed by Eq. (1) is to be considered as a convolution of three partial dimerizations leading to the individual isomeric forms.

2. ENERGY FITTING

If we consider the dimer as an equilibrium mixture of the three isomers (i.e., as one pseudospecies), dimerization, given by Eq. (1), is described by its overall equilibrium constant K_p simply related to the partial (one-isomer) equilibrium constants $K_{\mathrm{p},i}$:

$$K_\mathrm{p} = \sum_{i=1}^{3} K_{\mathrm{p},i} \tag{2}$$

where i stands for the C_2, C_s, or C_1 isomer. Molecular geometries and harmonic vibrational frequencies are generally produced by quantum-chemical calculations with a higher reliability than the energetics itself. Consequently, standard-thermodynamic potential terms based on the quantum-chemical parameters can be considered as quite reliable. The dimerization ground-state energy changes $\Delta H^\circ_{0,i}$ [i.e., the standard enthalpy changes at the zero temperature connected with processes expressed by

Eq. (1) for just one of the isomers], which represent a less certain part, can be obtained from fitting in order to obtain a best reproduction of observed equilibrium constants $K_p^{(\text{exp})}$. Thus, the partial equilibrium constants $K_{p,i}$ are considered [21] as functions of the (calculated) standard thermodynamic-potential changes and of the (fitted) enthalpy terms $\Delta H_{0,i}^{\circ}$. Let us mention for completeness that the standard thermodynamic potential of the radical ClO itself has for our purposes been evaluated using observed parameters [22–24].

A fit of the $\Delta H_{0,i}^{\circ}$ terms can be carried out with least squares. A local minimum of a convenient functional form, Λ, is to be found, e.g.,

$$\Lambda = \sum_T [\ln K_p^{(\text{exp})} - \ln K_p]^2 \tag{3}$$

where the summation runs over the observed temperatures. Similarly, one can optimize the differences in the Gibbs energy, i.e., in $RT \ln K_p$ terms:

$$\Lambda = \sum_T [RT \ln K_p^{(\text{exp})} - RT \ln K_p]^2 \tag{4}$$

or in other functional forms. In any case, the conditions of stationarity with respect to the ground-state energy changes $\Delta H_{0,i}^{\circ}$ ($i = 1$, 2, or 3) are to be fulfilled:

$$\left(\frac{\partial \Lambda}{\partial \Delta H_{0,i}^{\circ}}\right)_{\text{o}} = 0 \tag{5}$$

Numerical details of the fitting procedure will be given elsewhere [21].

The observed equilibrium constants $K_p^{(\text{exp})}$ are available as follows. In addition to one value measured by Basco and Hunt [5] at room temperature, Cox and Hayman [6] reported values for nine temperatures between 233 and 303 K. Thus, each of the functional forms [ln or RTln; see Eq. (3) or (4), respectively] was supplied with either nine observed K_p values [6] or with the latter set extended by the sole experimental K_p value [5]. It has turned out [21] that the fitting is numerically stable only in the two-dimensional case, i.e., after abandoning the C_1 species (as the isomer is not relevant in the temperature interval considered in the observations). For purposes of the present thermodynamic study, the $\Delta H_{0,3}^{\circ}$ term was purely evaluated from quantum-chemical data [18, 20]. Table I surveys the results of the two-dimensional fitting [21].

3. $Cl_2O_2(g)$ ISOMERIC INTERPLAY

Before evaluating the dimerization thermodynamics expressed by Eq. (1) within the fitted energetics, the interplay of the Cl_2O_2 isomers

Table I. Survey of the ClO Dimerization Energetics[a] Fitting [21] for Two Cl_2O_2 Isomers (Variation in the Optimized-Function Form[b] and/or Extent of Observed Data Employed[c])

Optimized term[b]	Number of points[c]	$\Delta H^{\circ}_{0,1}$[a] (kJ · mol^{-1})	$\Delta H^{\circ}_{0,2}$[a] (kJ · mol^{-1})	Acronym
ln	9	−67.72	−68.18	ln/9
	10	−68.87	−67.41	ln/10
RT ln	9	−69.53	−66.64	RT ln/9
	10	−70.01	−65.27	RT ln/10

[a] Ground-state energy changes (i.e., enthalpy changes at the absolute zero temperature) $\Delta H^{\circ}_{0,i}$ for dimerization to ClOOCl (C_2 symmetry; $\Delta H^{\circ}_{0,1}$) or $ClClO_2$ (C_s; $\Delta H^{\circ}_{0,2}$).

[b] Either sum of squares of calculation-observation differences in $\ln K_p$ or $RT \ln K_p$ was considered in the optimization (K_p stands for the ClO overall dimerization equilibrium constant).

[c] Either the nine-membered set of experimental equilibrium constants K_p [6] or its extension by the sole value [5] was employed.

themselves should be studied first. Let us consider mole fractions w_i of the three isomers in their equilibrium mixture. In terms of the partition functions q_i [with respect to the information available, they are of the usual rigid rotor and harmonic oscillator (RRHO) quality], the relative populations w_i in the three-membered isomeric mixture are given by [25–27]

$$w_i = \frac{q_i \exp[-\Delta H^{\circ}_{0,i}/(RT)]}{\sum_{j=1}^{3} q_j \exp[-\Delta H^{\circ}_{0,j}/(RT)]} \tag{6}$$

When treating thermodynamics of an equilibrium isomeric mixture, two types of quantities [25–27] can be employed, *viz.*, partial and overall terms. The standard partial terms ΔX°_i belong to processes dealing with the individual isomers; the overall terms ΔX°_T, to processes in which the equilibrium isomeric mixture acts as one pseudospecies. In addition to the partial and overall terms, a third quantity has been introduced [25–27]—the so-called isomerism contributions to thermodynamic terms, δX_1, related to the reference structure 1, defined as

$$\delta X_1 = \Delta X^{\circ}_T - \Delta X^{\circ}_1 \tag{7}$$

It is convenient to employ the species most stable in the low-temperature region as the reference structure.

Let us illustrate Eq. (7) on the heat capacity at constant pressure C_p; it holds that

$$\delta C_{p,1} = \delta C_{p,w,1} + \frac{1}{RT^2}\left[\sum_{i=1}^{3} w_i(\Delta H_i^\circ - \Delta H_1^\circ)^2 - (\delta H_1)^2\right] \tag{8}$$

where $\delta C_{p,w,1}$ stands for the so-called isofractional (i.e., based on hypothetical temperature-independent w_i weight factors) isomerism contribution to heat capacity:

$$\delta C_{p,w,1} = \sum_{i=1}^{3} w_i(\Delta C_{p,i}^\circ - \Delta C_{p,1}^\circ) \tag{9}$$

while the isomerism contribution to enthalpy is simply given by

$$\delta H_1 = \sum_{i=1}^{3} w_i(\Delta H_i^\circ - \Delta H_1^\circ) \tag{10}$$

The temperature evolution of the relative populations w_i in the three-membered Cl_2O_2 system based on the fitted energetics from Table I is given in Figs. 1–4. In fact, four sets of the ground-state energy changes

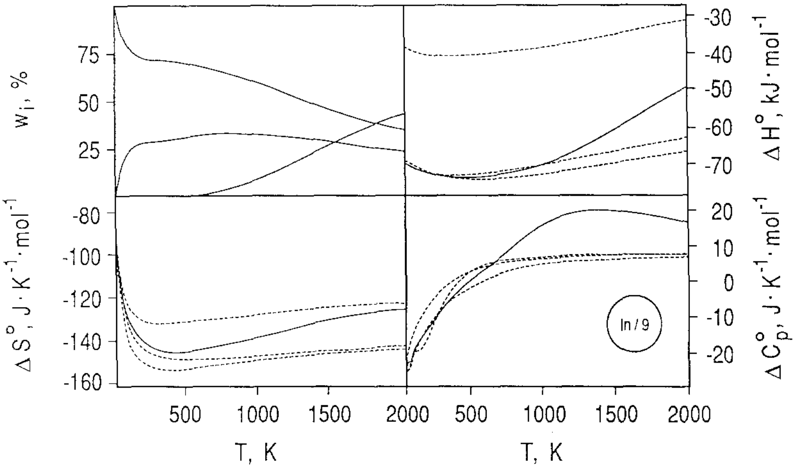

Fig. 1. Temperature dependence of the standard partial (dashed curves) and overall terms for the ClO(g) dimerization within the ln/9 (cf. Table I) energetics. Upper left: the weight factors w_i in three-membered isomeric set of the dimers; the ordering at the highest presented temperature (from top to bottom): C_1, C_s, C_2. Upper right: the standard enthalpy terms (ΔH°); the ordering of the partial terms at the highest presented temperature (from top to bottom): C_1, C_2, C_s. Lower left: the standard entropy terms (ΔS°); the ordering of the partial terms at the highest presented temperature (from top to bottom): C_1, C_s, C_2. Lower right: the standard heat capacity at constant pressure terms (ΔC_p°); the ordering of the partial terms at the highest presented temperature (from top to bottom): C_2, C_1, C_s. For the standard-state specification, cf. Tables II and III.

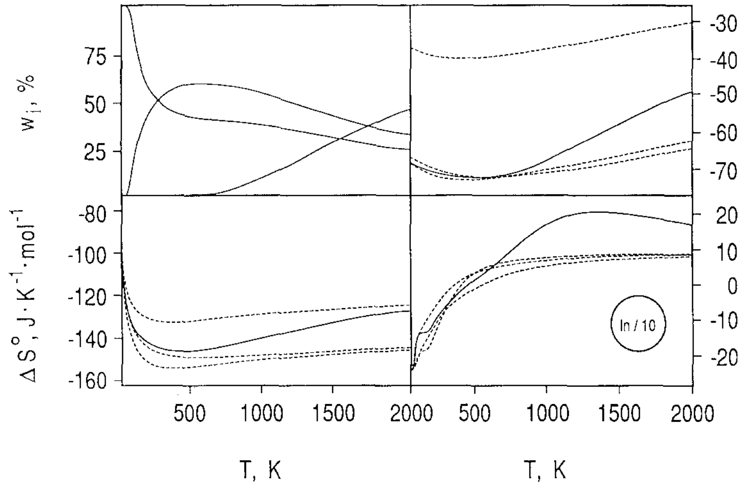

Fig. 2. Temperature dependence of the standard partial (dashed curves) and overall terms for the ClO(g) dimerization within the ln/10 (cf. Table I) energetics (for details see the legend to Fig. 1). The ordering of curves at the highest considered temperature is the same as specified in the legend to Fig. 1.

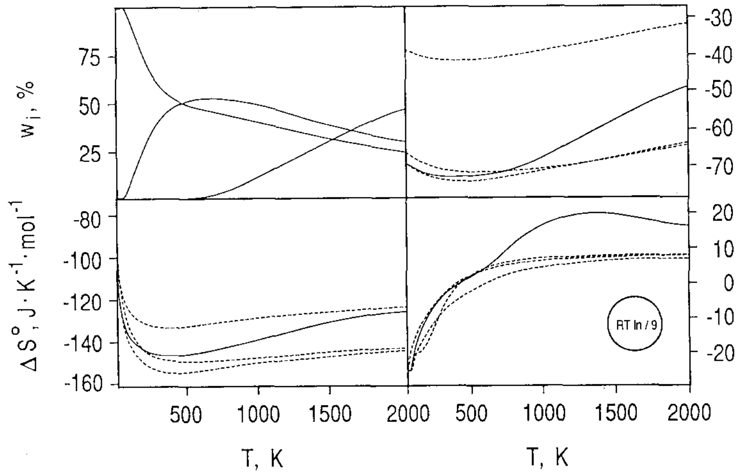

Fig. 3. Temperature dependence of the standard partial (dashed curves) and overall terms for the ClO(g) dimerization within the RT ln/9 (cf. Table I) energetics (for details see the legend to Fig. 1). The ordering of curves at the highest considered temperature is the same as specified in the legend to Fig. 1.

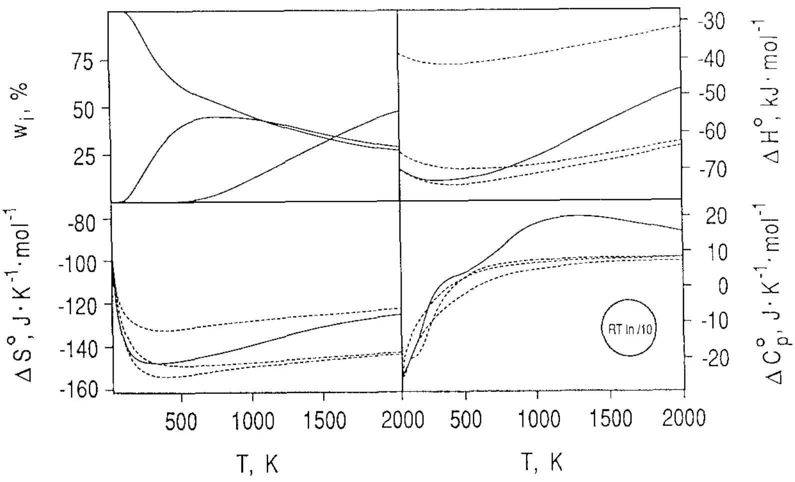

Fig. 4. Temperature dependence of the standard partial (dashed curves) and overall terms for the ClO(g) dimerization within the RTln/10 (cf. Table I) energetics (for details see the legend to Fig. 1). The ordering of curves at the highest considered temperature is the same as specified in the legend to Fig. 1.

$\Delta H^{\circ}_{0,i}$ are treated, of which the set coded by ln/9 is qualitatively different (interchange of the energy order at the absolute zero temperature between the C_2 and the C_s isomers).

In all the cases, nevertheless, the C_1 isomer (the highest in the potential energy [20]) is significantly populated at higher temperatures (and, finally, becomes the most populated species of the three structures). In three of the four considered energy sets there is a relative stability interchange between C_2 and C_s isomers. Its position is quite sensitive to the energetics (as can be seen in Table II). The stability interchanges can be also reflected in the isomerism contributions to heat capacity $\delta C_{p,1}$, *viz.*, in a striking course with two temperature maxima (Table II specifies the maxima). The isomerism contribution is, however, not a directly measurable quantity and therefore Table II includes the maximum in the standard overall heat capacity C_p° for the three-membered equilibrium Cl_2O_2 mixture. The second temperature maximum of the $\delta C_{p,1}$ term is well conserved in the overall term.

4. EVALUATION OF THE ClO(g) DIMERIZATION THERMODYNAMICS

The fitted energetics and the RRHO partition functions supplied with calculated [18, 20] molecular parameters of the dimeric species

Table II. Characterization of Some Distinguished[a] Points of the Cl_2O_2 Isomeric Interplay

Energy[b]	Type[a]	T (K)	w_1[c] (%)	w_2[c] (%)	w_3[c] (%)	$\delta C_{p,1}$[d] ($J \cdot K^{-1} \cdot mol^{-1}$)	C_p° ($J \cdot K^{-1} \cdot mol^{-1}$)	$\delta C_{p,1}/C_p^\circ$ (%)
ln/9	Cross	1530	44.3	27.9	27.9	12.8	93.8	13.6
	Cross	1831	37.6	24.8	37.6	10.4	92.1	11.3
	M:$\delta C_{p,1}$	27	94.2	5.8	3×10^{-60}	2.0	35.4	5.8
	M:$\delta C_{p,1}$	1274	51.1	30.5	18.3	13.8	94.0	14.7
	M:C_p°	1372	48.4	29.5	22.1	13.7	94.2	14.5
	M:%	26	94.3	5.7	8×10^{-61}	2.0	35.4	5.8
	M:%	1256	51.6	30.7	17.7	13.8	93.9	14.7
ln/10	Cross	248	50.0	50.0	9×10^{-5}	1.0	61.0	1.7
	Cross	1530	29.7	40.6	29.7	11.3	93.4	12.1
	Cross	1733	27.1	36.4	36.4	9.8	92.1	10.7
	M:$\delta C_{p,1}$	67	87.9	12.1	1×10^{-22}	5.7	44.3	13.0
	M:$\delta C_{p,1}$	1279	33.3	46.5	20.2	12.2	93.9	13.0
	M:C_p°	1334	32.5	45.1	22.4	12.2	93.9	13.0
	M:%	62	89.7	10.3	2×10^{-24}	5.7	43.8	13.0
	M:%	1270	33.4	46.7	19.9	12.2	93.8	13.0
RT ln/9	Cross	495	49.9	49.9	0.2	−0.4	74.1	−0.5
	Cross	1530	31.0	37.9	31.0	11.0	93.1	11.8
	Cross	1660	29.1	35.5	35.5	10.0	92.3	10.9
	M:$\delta C_{p,1}$	150	84.1	15.9	6×10^{-9}	6.9	55.2	12.4
	M:$\delta C_{p,1}$	1245	36.0	43.9	20.1	12.2	93.7	13.0
	M:C_p°	1302	34.9	42.7	22.4	12.1	93.8	12.9
	M:%	134	87.5	12.5	3×10^{-10}	6.7	53.0	12.7
	M:%	1237	36.1	44.1	19.8	12.2	93.7	13.0
RT ln/10	Cross	1135	41.4	41.4	17.1	12.2	93.5	13.1
	Cross	1530	32.7	34.5	32.7	10.7	92.7	11.5
	Cross	1565	32.1	34.0	34.0	10.4	92.5	11.2
	M:$\delta C_{p,1}$	216	87.6	12.4	1×10^{-5}	7.0	63.5	11.1
	M:$\delta C_{p,1}$	1197	39.9	40.4	19.7	12.3	93.7	13.1
	M:C_p°	1256	38.5	39.3	22.2	12.2	93.8	13.0
	M:%	198	90.0	10.0	3×10^{-6}	6.9	61.3	11.3
	M:%	1188	40.1	40.5	19.3	12.3	93.7	13.1

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

[b] See Table I for the acronym meaning.

[c] The mole fraction of the species in the equilibrium isomeric mixture; 1, 2, and 3 denote the C_2, C_s, and C_1 isomer, respectively (C_s, C_2, and C_1 in the ln/9 energetics).

[d] Isomerism contribution to heat capacity related to the species most stable in the very low-temperature region, i.e., to the C_2 isomer (to C_s in the ln/9 energetics).

(and observed parameters [22–24] for the monomer) allow the dimerization (1) thermodynamics to be evaluated in a broad temperature interval. Again, not only partial but also overall standard thermodynamic changes are to be calculated. The temperature dependences of the standard partial and overall enthalpy, entropy, and heat capacity at constant pressure

Table III. Temperature Dependences of the Calculated Standard[a] Partial Changes in Enthalpy $\Delta H^\circ_{T,i}$ (Evaluated in the $RT\ln/9$ Energetics[b]), Entropy $\Delta S^\circ_{T,i}$, and Heat Capacity at Constant Pressure $\Delta C^\circ_{p,T,i}$ for the ClO(g) Individual Dimerizations and of the Partial Equilibrium Constant $K_{p,i}$

Dimerization to[b]	T (K)	$\Delta H^\circ_{T,i}$ (kJ · mol^{-1})	$\Delta S^\circ_{T,i}$ (J · K^{-1} · mol^{-1})	$\Delta C^\circ_{p,T,i}$ (J · K^{-1} · mol^{-1})	$\log K_{p,i}$ $\{K_p\} = (\mathrm{atm}^{-1})$
ClOOCl(C_2; g)	100	−71.7	−139	−19.5	30.2
	150	−72.7	−147	−16.9	17.6
	200	−73.4	−151	−12.3	11.3
	250	−73.9	−153	−7.69	7.44
	300	−74.2	−154	−4.04	4.86
	400	−74.3	−155	0.66	1.63
	500	−74.1	−154	3.24	−0.31
	1000	−71.3	−150	7.00	−4.13
	1500	−67.5	−147	7.73	−5.34
	2000	−63.6	−145	7.99	−5.92
ClClO$_2$(C_s; g)	100	−68.9	−134	−17.6	29.0
	150	−69.7	−140	−14.2	16.9
	200	−70.3	−144	−11.0	10.8
	250	−70.8	−146	−8.53	7.15
	300	−71.1	−148	−6.57	4.67
	400	−71.6	−149	−3.51	1.57
	500	−71.9	−150	−1.10	−0.31
	1000	−70.6	−148	4.86	−4.05
	1500	−67.7	−146	6.64	−5.26
	2000	−64.1	−144	7.34	−5.83
ClOClO(C_1; g)	100	−40.3	−125	−12.2	14.5
	150	−40.9	−129	−8.95	7.48
	200	−41.2	−131	−5.85	3.90
	250	−41.5	−133	−3.32	1.74
	300	−41.6	−133	−1.42	0.30
	400	−41.6	−133	1.17	−1.51
	500	−41.4	−132	2.88	−2.60
	1000	−38.8	−129	6.45	−4.72
	1500	−35.3	−126	7.42	−5.37
	2000	−31.5	−124	7.80	−5.66

[a] The standard-state choice: an ideal gas at 1 atm = 101325 Pa pressure.

[b] Compare Table I; the ground-state energy changes: $\Delta H^\circ_{0,i} = -69.53$, -66.64, or -38.57 kJ · mol^{-1} for dimerization to ClOOCl, ClClO$_2$, or ClOClO, respectively.

changes for the dimerization are given in Figs. 1–4 for the four fitted energetics from Table I. All terms are quite strongly temperature dependent. A quite unusual temperature evolution (including a temperature maximum) is exhibited by the standard overall heat capacity change $\Delta C_\mathrm{p}^\circ$ (i.e., the temperature maximum in the standard heat capacity C_p° of the equilibrium mixture of the isomeric dimers reported in Table II is conserved even after transition to the dimerization changes).

For further application purposes, one of the four fitted energetics should be recommended. The following reasoning can be applied. As the observed K_p values [6] exhibit lower experimental error at higher temperatures, it seems reasonable to prefer the $RT\ln$ functional form represented by Eq. (4) over the ln one represented by Eq. (3) (owing to the convenient weighting factor RT present in the former case). Moreover, the single experimental value [5] does not seem to be consistent with the values [6], as its inclusion substantially increases the residual sum of squares in the fitting treatment [21]. Hence, it follows that the $RT\ln/9$ energetics should be recommended as the most reliable. The latter energetics has been employed in the final evaluation of the dimerization thermodynamics at both partial (Table III) and overall (Table IV) level. The results in Tables III and IV represent a refined, recommended set for further applications, including elucidation and evaluation of ozone-depletion mechanisms.

Table IV. Temperature Dependences of the Calculated Standard[a] Overall Changes in Enthalpy ΔH_T°, Entropy ΔS_T°, and Heat Capacity at Constant Pressure $\Delta C_{p,T}^\circ$ for the ClO(g) Total Dimerization and of the Overall Equilibrium Constant K_p, Derived from the Partial Values in Table III

T (K)	ΔH_T° (kJ · mol^{-1})	ΔS_T° (J · K^{-1} · mol^{-1})	$\Delta C_{p,T}^\circ$ (J · K^{-1} · mol^{-1})	$\log K_p$ $\{K_p\} = (\mathrm{atm}^{-1})$
100	71.6	137	−14.3	30.2
150	−72.2	−142	−10.0	17.7
200	−72.6	−144	−6.37	11.4
250	−72.8	−145	−3.79	7.62
300	−73.0	−146	−2.08	5.08
400	−73.1	−146	0.36	1.90
500	−72.9	−146	2.90	−0.01
1000	−67.5	−139	17.6	−3.74
1500	−57.9	−131	18.9	−4.84
2000	−49.3	−126	15.5	−5.31

[a] The standard-state choice: an ideal gas at 1 atm = 101,325 Pa pressure.

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