An evaluation of $CO_2/(CO_2)_2$ equilibrium populations in the planetary atmosphere close to the surface of Mars or Venus [α,β]

Zdeněk Slanina [1]

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

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Abstract

The thermodynamics of carbon dioxide dimerisation is evaluated using partition functions supplied with calculated molecular parameters and energetics. The evaluated dimerisation equilibrium constant is applied to estimation of the dimer populations in its equilibrium mixture with the monomer under the planetary atmosphere conditions close to the surface of Mars and Venus. For Mars the predicted $(CO_2)_2$ mole fraction (in the two-component mixture with CO_2) amounts to 0.0019% or 0.016%, depending on the potential energy approximation, i.e. considerably lower values than in a previous simplified treatment. However, in the case of Venus, it reaches 13.1% or even 22.9%, i.e. two orders of magnitude higher than in the simplified approach. This suggests that the dimer should play an important role in modelling the thermal properties of the atmosphere of Venus.

INTRODUCTION

The carbon dioxide dimer $(CO_2)_2$ has been the subject of constant research interest [2–20] (both experimental and computational), this also being true, to some extent, for its ionised states [21–24]. Nevertheless, the dimer characterisation and its understanding are far from being complete —even its structure (complicated by a possible isomerism [11–13]) has not been perfectly clarified. In addition to laboratory observations, Nature offers a large-scale experimental medium in the form of planetary atmospheres [25–29], especially those of Mars and Venus. Carbon dioxide forms 95.3 and 96.5 vol.% of the Mars and Venus atmospheres, respectively [28].

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[β] Part LXVI in the series Multi-Molecular Clusters and Their Isomerism; for Part LXV, see ref. 1.
[1] 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.

TABLE 1

Survey of the $(CO_2)_2$ formation energetics [a]

Process	Ref.	ΔE	$\Delta H_0^{\ominus}$
$2CO_2(g) = (CO_2)_2(C_{2h})(g)$	20	-4.18	-3.14
$2CO_2(g) = (CO_2)_2(C_{2h})(g)$	11	-9.75	-8.27
$2CO_2(g) = (CO_2)_2(C_{2v})(g)$	11	-5.86	-4.88

[a] Either the potential energy change ΔE or the ground-state energy change $\Delta H_0^{\ominus}$ for the $CO_2(g)$ dimerisation, both in kJ mol^{-1}.

This article reports the state-of-the-art calculations of the dimer proportions in its equilibrium mixture with the monomer.

COMPUTATIONS

We shall employ two recent quantum chemical calculations. Brigot et al. [11] found two energy-minimum structures, the parallel and T-form, possessing C_{2h} and C_{2v} point-group symmetries, respectively (the C_{2h} species being almost 4 kJ mol^{-1} lower in energy, see Table 1). However, Eggenberger et al. [20], using a large basis set and correlation evaluation, confirmed only one energy-minimum structure, namely the C_{2h} species, and found it to be less stable than in the older calculations [11] (see Table 1). In the present treatment, both sets [11,20] of energetics and molecular parameters will be studied.

Partition functions were constructed [30] in the usual rigid-rotor and harmonic-oscillator (RRHO) approximation and the thermodynamics of the association

$$2CO_2(g) = (CO_2)_2(g) \tag{1}$$

was evaluated. In particular, the equilibrium constant

$$K_p = \frac{p_{(CO_2)_2}}{p_{CO_2}^2} \tag{2}$$

was calculated, where p_i denotes the partial pressures of the monomer and dimer. With the data of ref. 11, the isomerism in the dimer must be taken into account, i.e. in addition to two partial equilibrium constants, the overall term for the total CO_2 dimerisation is also introduced:

$$K_p(\text{total}) = K_p(C_{2h}) + K_p(C_{2v}) \tag{3}$$

The isomerism at the level of the standard thermodynamic terms is treated within the weighting treatment [30].

The composition of the equilibrium monomer–dimer mixture can be described by the mole fractions x_1 and x_2 ($x_1 + x_2 = 1$ or 100%). At the

TABLE 2

Calculated CO_2 dimerisation standard [a] enthalpy $\Delta H_T^{\ominus}$ and entropy $\Delta S_T^{\ominus}$, and the equilibrium constant $K_p = p_{(CO_2)_2}/p_{CO_2}^2$ at Mars and Venus surface temperatures [b]

Process	ΔE ref. source	T [b] (K)	$\Delta H_T^{\ominus}$ (kJ mol^{-1})	$\Delta S_T^{\ominus}$ (J K^{-1} mol^{-1})	K_p (atm^{-1})
$2CO_2(g) = (CO_2)_2(C_{2h})(g)$	20	200	-2.44	-59.7	0.00329
$2CO_2(g) = (CO_2)_2(C_{2h})(g)$		733	1.95	-49.1	0.00198
$2CO_2(g) = (CO_2)_2(C_{2h})(g)$	11	200	-7.94	-73.9	0.0165
$2CO_2(g) = (CO_2)_2(C_{2v})(g)$			-4.13	-57.3	0.0122
$2CO_2(g) = (CO_2)_2(total)(g)$			-6.32	-61.1	0.0287
$2CO_2(g) = (CO_2)_2(C_{2h})(g)$	11	733	-3.61	-63.4	0.000885
$2CO_2(g) = (CO_2)_2(C_{2v})(g)$			0.255	-46.6	0.00351
$2CO_2(g) = (CO_2)_2(total)(g)$			-0.523	-45.8	0.00440

[a] The standard state: ideal gas phase at 101 325 Pa pressure.
[b] Estimated temperatures [28]: Mars, 200 K; Venus, 733 K.

total pressure P, for the dimer mole fraction [31]

$$x_2 = \frac{2PK_p + 1 - (4PK_p + 1)^{1/2}}{2PK_p} \tag{4}$$

For our purposes the surface temperatures of Mars and Venus will be approximated by 200 and 733 K, respectively [28]. The total pressures P of the monomer/dimer equilibrium mixture are derived from the total planetary atmosphere pressure close to the surface scaled by the volume ratio [28] of the carbon dioxide. In this way, total pressures P of about 0.006 and 87.6 atm for the surface of Mars and Venus, respectively, can be generated.

RESULTS AND DISCUSSION

Table 2 gives the standard enthalpy $\Delta H_T^{\ominus}$ and entropy $\Delta S_T^{\ominus}$ changes, and the equilibrium constants for dimerisations (eqn (1)) based on the data in ref. 20 (C_{2h} structure alone) and in ref. 11 (two dimeric structures, partial and overall terms). Owing to the differences in the energetics (Table 1), the differences in the K_p values between the two treatments are substantial. However, with respect to the present state of quantum-chemical methodology, a simple indication of the more reliable data is difficult. We can, instead, consider both sets of results as an indication of an interval within which the true values can lie. The application of the RRHO approximation is not important in the case of Mars because of the low temperature at the surface; however, it may be important for Venus. However, an evaluation of the corrections to the RRHO behaviour has so far been prohibited by computational demands.

The mole fractions x_2 of the dimer in the $CO_2/(CO_2)_2$ equilibrium mixture under the conditions believed to exist close to the surface of Mars

TABLE 3

Calculated mole fraction x_2 of $(CO_2)_2$ in its equilibrium mixture with CO_2 at Mars and Venus surface conditions

Planet	ΔE ref. source	T (K) [a]	p (atm) [b]	x_2 (%)
Mars	20	200	0.006	0.0019
	11			0.016
Venus	20	733	87.6	13.1
	11			22.9

[a] Estimated surface temperatures [28].
[b] Estimated surface pressures [28].

and Venus [28] are given in Table 3. There are, in fact, two effects interacting here—the destabilisation caused by a temperature increase can be overcompensated for by a sufficiently high pressure increase. This compensation mechanism works well in the Venus case, producing considerably high estimations of the dimer mole fraction. Clearly, such high dimer fractions would influence the thermal properties of the Venus atmosphere and should be taken into account in their modelling. In contrast to Venus, in the case of Mars the total pressure P is too low and, consequently, the dimer mole fraction is suggested to be lower by several orders of magnitude.

In a recent study [26], the dimer fractions were evaluated in a simplified approach based on the treatment suggested by Stogryn and Hirschfelder [32]. The treatment is based on a simple Lennard-Jones scheme (although it somehow takes potential anharmonicity into account). Moreover, a uniform molal density was employed [26] which does not correspond well to the real pressure conditions. It is therefore not surprising that the previous values are substantially different from the data of this report (our data are considerably lower for Mars and much higher for Venus). However, if we repeat the treatment in ref. 32 using a more realistic gas density, a better agreement is obtained (about 4% of the dimer mole fraction for Venus).

The relatively high populations of $(CO_2)_2$ in the Venus atmosphere should, for example, lead to a heat capacity increase. One source of enhancement originates in the dimer low-frequency vibrations, i.e. the intermolecular terms that are absent with free monomers. Another source could be related to temperature changes in composition, i.e. the so-called relaxation effects, so far almost totally ignored (throughout all thermodynamic applications). A detailed study of the particular conditions on Venus is necessary for further space-research studies.

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