

THE DIMER (HCl)₂: STATIONARY POINTS
ON THE SCF 4-31G ENERGY HYPERSURFACE
AND THE ROLE OF ENTROPY
IN THE DIMER FORMATION

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

Two stationary points have been investigated on the 4-31G SCF energy hypersurface of (HCl)₂. It has been shown, in agreement with experiment, that only the quasilinear structure satisfies all criteria required for a real minimum. Small heat of reaction and the crucial role of entropy in the (HCl)₂ formation suggest that the dimer (HCl)₂, in contrast to (HF)₂, represents a true van der Waals molecule. A very small energy difference between the two stationary points (minimum and saddle point) suggests a very high rate of interconversion between two possible structures of the quasilinear form. Common features of and differences between (HCl)₂ and (HF)₂ are pointed out.

Recently two stationary points were found on the 4-31G energy hypersurface of the dimer (HF)₂. These corresponded to a quasilinear and a cyclic structures. The former was demonstrated to be a real minimum and the latter was supposed to be a saddle point¹. Nonempirical calculations of the same type on (HCl)₂ favoured^{2,3} again, on energy grounds, the quasilinear structure over the cyclic one. The nature of the stationary points, however, was not analyzed in the papers cited^{2,3}. In contrast to (HF)₂, the experimental evidence on the structure of (HCl)₂ is not so conclusive. Nevertheless, Girardet and Robert^{4,5} as well as Schriver and co-workers⁶ were able to show spectroscopically the non-equivalence of subsystems constituting the (HCl)₂ dimer and concluded that the axes of the HCl molecules are almost orthogonal.

It is well known that the passage from a compound consisting of first row elements to an analog containing a heavier element is frequently associated with considerable changes of some chemical properties. We have been wondering whether this also applies to the pair (HF)₂ and (HCl)₂. Hence, the purpose of this paper is threefold: 1) to investigate the nature of stationary points of (HCl)₂, 2) to treat thermodynamically the formation of the dimer, and 3) to comment on the rate of interconversion of the two structurally equivalent forms of the dimer. Finally, comparison is made for the (HF)₂ and (HCl)₂ dimers.

CALCULATIONS

The nonempirical SCF method using the STO 4-31G basis set⁷ was used in all computations. The function counterpoise correction^{8,9}, $\Delta\epsilon$, was applied, the corrected stabilization energy, $\Delta E'$, being then the sum of ΔE and $\Delta\epsilon$. Dispersion energy was estimated by means of the semi-empirical potential¹⁰. The coordinates assumed in the vibrational FG treatment are visualized in Fig. 1. Thermodynamic characteristics of equilibrium and rate processes were obtained by standard procedures previously described in detail¹¹. The geometries of the stationary points found are within 0.2 pm and 1°.

RESULTS AND DISCUSSION

Our attention focused on two among various possible structures of the dimer (HCl)₂, namely on the quasilinear and cyclic forms. The optimum bond lengths, bond angles, and stabilization energies obtained for them are summarized in Table I. The optimum bond length of HCl amounts to 0.1299 nm. The equilibrium geometry and dimer stabilization energy of the linear form are in fair agreement with published theoretical data^{2,3}. Experimentally found⁴⁻⁶ separation of subsystems (0.355–0.361 nm; quasi-

TABLE I

Geometry and Stabilization Energy for Linear and Cyclic Structures of the (HCl)₂ Dimer Given by 4-31G Calculations (bond lengths in nm, angles in degrees)

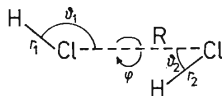
Structure ^a	r_1	r_2	R	ϑ_1	ϑ_2	φ	ΔE kJ/mol	$\Delta E'$ kJ/mol ^b
Linear	0.130	0.130	0.3986	102	7	180	-8.838	-5.808
Cyclic	0.130	0.130	0.3774	55	55	180	-7.075	-3.321

^a Cf. Fig. 1; ^b For the definition, see text.

FIG. 1

Internal Coordinates for the Quasilinear and Cyclic Structures of (HCl)₂

For the cyclic form we assumed the following symmetry coordinates: $S_1(A_g) = 1/\sqrt{2}(r_1 + r_2)$; $S_2(A_g) = R$; $S_3(A_g) = 1/\sqrt{2}(\vartheta_1 + \vartheta_2)$; $S_4(B_u) = 1/\sqrt{2}(r_1 - r_2)$; $S_5(B_u) = 1/\sqrt{2}(\vartheta_1 - \vartheta_2)$; $S_6(A_u) = \varphi$.



linear structure assumed) is shorter than that predicted by the SCF calculations. This difference may be ascribed to the small basis set used and to the neglect of correlation energy. The second effect might be anticipated to be rather large owing to the polarisability of chlorine atoms. However, if use is made of C_6 , C_8 and C_{10} coefficients given by Fontana¹⁰, estimates of dispersion energy for $(\text{HCl})_2$ suggest the opposite. Namely, for the $\text{Cl}\cdots\text{Cl}$ distance of 0.3986 nm, where the dispersion energy should approximate reasonably the correlation energy, the dispersion energy becomes -2.03 kJ/mol, which is only about a quarter of the SCF stabilization energy obtained for the dimer. As regards the absolute value of the stabilization energy, the computed $\Delta E'$ is 5.8 kJ/mol, compared to the experimental value¹² of 8.9 kJ/mol.

In order to be able to distinguish between minima and saddle points on the $(\text{HCl})_2$ energy hypersurface we performed the vibrational FG analysis¹³ for the critical structures. The calculated harmonic force constants for these structures are presented in Table II.

With the quasilinear structure all eigenvalues were positive, *i.e.* this form represents a real minimum on the $(\text{HCl})_2$ energy hypersurface (Table III). With the cyclic form, however, we obtained one negative eigenvalue which means that this stationary point is a saddle point. Recently, Kerns and Allen¹⁵ suggested that the cyclic form represented a saddle point; complete vibrational analysis was not performed, however

TABLE II

Harmonic Force Constants for the Linear and Cyclic Structure of the $(\text{HCl})_2$ Dimer Given by 4-31G Calculations

Structure ^a	Force constants ^b						
Linear	$F_{r_1 r_1}$	$F_{r_2 r_2}$	F_{RR}	$F_{\theta_1 \theta_1}$	$F_{\theta_2 \theta_2}$	$F_{\phi \phi}$	$F_{r_1 r_2}$
	4.531	4.489	0.059	0.038	0.071	0.001	-0.001
	$F_{R \theta_1}$	$F_{R \theta_2}$	$F_{\theta_1 \theta_2}$				
	-0.005	0.002	0.035				
Cyclic	F_{11}	F_{22}	F_{33}	F_{44}	F_{55}	F_{66}	F_{12}
	4.518	0.066	0.060	4.509	-0.006	0.011	-0.010
		4.518	0.066	0.060			
	F_{13}	F_{23}	F_{34}				
	-0.064	0.010	0.0				

^a Cf. Fig. 1; ^b Units for force constants: stretching -10^2 N m⁻¹, bending -10^{-18} N m rad⁻², bend-stretch -10^{-8} N rad⁻¹.

In contrast to what may be expected about the SCF predictions for stretching modes, the calculated harmonic wavenumber of HCl is lower than the observed one. The same trend was found¹ with the 4-31G harmonic frequency of HF.

The predictions made for the intermolecular modes with low wavenumbers are certainly open to large uncertainties. We believe, however, that their use is justifiable for purposes of semiquantitative estimates of thermodynamic characteristics.

Comment on the (HF)₂ dimer. Curtiss and Pople¹ have proved that the quasilinear structure represents a real minimum. They assumed that the cyclic form is a saddle point; the nature of this stationary point was not analyzed, however. Therefore, we decided to do that, in order to be able to make a conclusive comparison of (HCl)₂ and (HF)₂ structures. By using the above mentioned FG analysis we obtained a set of six vibrational frequencies and just one of them was negative. Hence, the cyclic structure of the (HF)₂ dimer is a saddle point. It may be concluded that the structures of (HF)₂ and (HCl)₂ are very similar.

Thermodynamics of (HCl)₂ formation. Calculated characteristics of the process (1) are summarized in Table IV.



They were obtained by means of partition functions computed from the 4-31G molecular constants. Rigid rotator, harmonic oscillator and ideal gas approximations

TABLE III
Computed and Observed Vibrational Wavenumbers (in cm⁻¹) for HCl and (HCl)₂

Species	Computed		Observed	
HCl	2 806		2 991 ^a	2 886 ^b
(HCl) ₂	quasilinear	cyclic		
	A' 2 801	A _g 2 798	2 856 ^c	
	A' 2 788	B _u 2 794	2 818 ^c	
	A' 308	A _g 244	—	
	A'' 263	A _u 183	—	
	A' 130	A _g 78	—	
	A' 71	B _u 78 ^d	—	

^a Harmonic, ref.¹⁴; ^b Fundamental, ref.¹⁴; ^c Measured in the Ar matrix, ref.⁶; ^d Imaginary frequency.

were adopted. By inspection of data given in Table IV it becomes evident that the $(\text{HCl})_2$ dimer is, in contrast to $(\text{HF})_2$, a true van der Waals molecule: the ΔG^0 value is positive even at 100 K (it would become negative after adding the value of dispersion energy noted above) and, at 298 K, ΔH^0 represents about 25% of $T\Delta S^0$. Previously we have pointed out¹⁶ the importance of the entropy term in estimating stabilities of van der Waals systems: with hydrogen bonded complexes we showed that the ΔH^0 and $T\Delta S^0$ terms are of a comparable magnitude. For the dimers dealt with in the present study, the $T\Delta S^0$ terms are rather close in absolute value, as it of course might be expected on the basis of similarity in structures of $(\text{HF})_2$ and $(\text{HCl})_2$. The ΔE values are largely different, however, so that with the $(\text{HF})_2$ formation ΔH^0 is considerably larger than $T\Delta S^0$, whereas with the $(\text{HCl})_2$ formation ΔG^0 is determined mainly by the $T\Delta S^0$ term and the process (*I*) may be called entropy controlled.

TABLE IV
Thermodynamic Characteristics of the $(\text{HCl})_2$ Formation^a
Values in parentheses concern the $(\text{HF})_2$ dimer.

<i>T</i> , K	ΔH^0 , kJ/mol	$T\Delta S^0$, kJ/mol	ΔG^0 , kJ/mol	log <i>K</i>
100	− 5.81 (−27.19)	− 7.19 (− 7.92)	1.38 (−19.27)	−0.72 (10.08)
298.2	− 5.46 (−28.48)	−21.21 (−26.22)	15.75 (− 2.27)	−2.76 (0.40)
500	− 4.12 (−27.92)	−33.88 (−43.29)	29.75 (15.37)	−3.11 (−1.70)

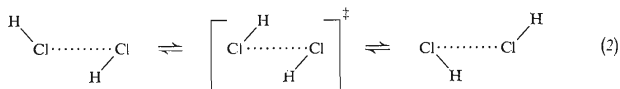
^a ΔE of the process $2 \text{HX} \rightleftharpoons (\text{HX})_2$ amounts to -8.84 and -33.47 kJ/mol for $\text{X} = \text{Cl}$ and F , respectively.

TABLE V
Activation Parameters (in kJ/mol) for the Interconversion between Two Possible Quasilinear Structures of $(\text{HCl})_2$ and $(\text{HF})_2$

Dimer	ΔE^\ddagger	ΔH_0^\ddagger	ΔH_{100}^\ddagger	$T\Delta S_{100}^\ddagger$
$(\text{HCl})_2$	1.76	0.21	0.02	−0.32
$(\text{HF})_2$	4.48	2.41	2.32	0.04

It should be noted that we examined¹⁷ the $T\Delta S^0$ terms with a large series of hydrogen bonded complexes and we were able to show that the linear relationship between ΔH^0 and $T\Delta S^0$ also holds with this type of compounds.

Rate of (HCl)₂ interconversion. Once the entries of Tables I and III are available, the absolute rate theory (ART) may be applied to the following process:



The calculated activation parameters are presented in Table V. The process is associated with a very small activation energy and therefore its rate constant is almost temperature-independent; $\log k$ amounts to 12.6 at 100 K and 12.7 at 500 K. For $\log k$ of the (HF)₂ interconversion we obtained 11.1, 12.3 and 12.6 at 100, 300 and 500 K, respectively.

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