

DIMERIZATION OF HOMONUCLEAR BIATOMIC MOLECULES

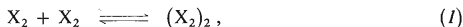
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Reversible dimerization of the type $2 X_2 \rightleftharpoons (X_2)_2$ ($X = N, O, Br, I$) were studied theoretically. The estimates of reaction enthalpies were based on the Buckingham potential. Entropy changes were calculated by means of statistical thermodynamics. Reasonable agreement between calculated and experimental data was found.

The subject of this paper is the calculation of equilibrium constants of the dimerization of homonuclear biatomic molecules:



where X stands for N, O, Br or I. Except for the oxygen dimerization they represent, at first sight, rather unusual interactions of closed-shell systems. In fact, however, these reactions are very well defined and not as unusual as they might seem. A treatment of the interaction by means of the simple MO (extended Hückel) method results, in agreement with chemical intuition, only in repulsion. However, any method capable of describing at least a fraction of the van der Waals interactions gives a minimum on the potential energy curve. Because an *ab initio* calculation followed by a complete configuration interaction treatment is prohibitively extensive for the systems under study, and because it is not known how far semiempirical methods of quantum chemistry account for van der Waals energies, estimates of enthalpy changes (Eq. (I)) were based on empirical methods.

Experimental studies of equilibria, mostly in the gas phase, have been performed with molecular nitrogen¹, oxygen^{2,3}, bromine⁴ and iodine⁵. The interaction between hydrogen molecules has been investigated theoretically at the *ab initio* level with complete configuration interaction⁶. An empirical method has been used with such molecules as Ar, Kr, CO₂ and CH₄ (ref. 7). Furthermore, an attempt has been made to calculate the dimerization energy of nitrogen molecules⁸.

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CALCULATIONS

A. Interaction Energy

Total interaction energy between two homonuclear molecules A and B can be obtained as a sum of attractive-dispersion and repulsion energies:

$$E_{\text{TOT}} = -C_1 \sum_i^A \sum_j^B \left(\frac{r_{ij}}{R_i + R_j} \right)^{-6} + C_2 \sum_i^A \sum_j^B \exp \left(-C_3 \frac{r_{ij}}{R_i + R_j} \right) \quad (2)$$

where C_1 , C_2 and C_3 are constants, i, j denote atoms, R_i and R_j are atomic van der Waals radii of atoms i and j , r_{ij} is the distance between atoms i and j . Calculations were performed with two sets of parameters (Table 1): Parameters 1, originally obtained by Kitajgorodskij⁹ were recalculated for sums of atomic radii instead of equilibrium distances. Atomic van der Waals radii were taken from ref.¹⁰. Parameters 2 were proposed by Eliel and coworkers¹¹. Moreover, interaction energies were calculated in the monopole-bond polarizabilities approximation^{12,13}, in which dispersion energy was evaluated by means of the London approximation involving the bond polarizability tensor. In the particular case of interaction between homonuclear molecules, the electrostatic and polarization contributions vanish. The bond polarizabilities used were taken from ref.¹⁴, except those for the I—I bond,* which were estimated from the known Cl—H, I—H and Cl—Cl bond polarizabilities¹⁴. The molecular "mean excitation energies", which appear in the London expression, were taken equal to 26.5 eV (ref.¹⁵). The formula and parameters for the repulsive term were the same as in the first case.

The geometry of cluster $(X_2)_2$ was obtained by minimizing the total interaction energy $E_{\text{TOT}}(r_{ij})$:

$$\frac{\partial E_{\text{TOT}}}{\partial r_{ij}} = 0 \quad (i, j = 1, 2). \quad (3)$$

If we express E_{TOT} from Eq. (3) in terms of the attractive-dispersion and repulsion energy, the following set of equations results:

$$\ln \left(\frac{r_{ij}}{R} \right) = \frac{C_3}{7} \frac{r_{ij}}{R} + \frac{1}{7} \ln \left(\frac{6C_1}{C_2 C_3} \right) \quad (i, j = 1, 2), \quad (4)$$

where $R = R_i + R_j$.

Evidently, if this set of four equations has a solution, all r_{ij} are identical: the cluster $(X_2)_2$ has a tetrahedral form of D_{2d} symmetry.

* The estimated values $\alpha_L = 13.87$ and $\alpha_T = 7.41 \text{ \AA}^3$ are somewhat lower than in ref.¹⁶.

Eq. (4) is easy to solve iteratively; it is possible to show that the necessary and sufficient condition for the existence of a minimum of the E_{TOT} function is:

$$-\ln\left(\frac{1}{7} \frac{C_3}{R}\right) > \frac{1}{7} \ln\left(\frac{6C_1R^7}{C_2C_3}\right) + 1. \quad (5)$$

In the case of Kitajgorodskij's parameters, values of C_1, C_2, C_3 are identical for all atoms of the periodic system; then r_{ij}/R must also be identical for all clusters $(X_2)_2$, and consequently the minimal interaction energy is also independent of the type of atom:

$$\frac{r_{ij}}{R} = 1.105, \quad (6)$$

$$E_{TOT} = -288.6 \text{ cal} \cdot \text{mol}^{-1}. \quad (7)$$

TABLE I

Parameters of Eq. (2) for Nitrogen, Oxygen, Bromine and Iodine Atoms
l and 2 denote parameters 1 and 2; cf. text.

Atom	$C_1, \text{kcal. mol}^{-1}$		$C_2, \text{kcal. mol}^{-1}$		C_3		$R, \text{\AA}$	
	<i>l</i>	2	<i>l</i>	2	<i>l</i>	2	<i>l</i>	2
N	0.2423	0.2138	30 100	78 660	11.8643	13.5870	1.6	1.5
O	0.2423	0.2610	30 100	96 048	11.8643	13.5870	1.5	1.4
Br	0.2423	0.9765	30 100	359 352	11.8643	13.5870	1.85	1.95
I	0.2423	1.4018	30 100	515 844	11.8643	13.5870	1.96	2.15

TABLE II

Calculated Molecular Constants of Dimers $(X_2)_2$
l and 2 denote parameters 1 and 2; cf. text.

Species	$r_{ij}, \text{\AA}$		$E_{TOT}, \text{cal. mol}^{-1}$		$f_r, \mu \text{ dyn. \AA}^{-1}$		$V_0, \text{cal. mol}^{-1}$	
	<i>l</i>	2	<i>l</i>	2	<i>l</i>	2	<i>l</i>	2
$(N_2)_2$	3.5	3.0	-289	-460	2.7	6.3	6	19
$(O_2)_2$	3.3	2.8	-289	-562	3.1	8.8	11	45
$(Br_2)_2$	4.1	3.9	-289	-2 103	2.0	16.9	73	692
$(I_2)_2$	4.3	4.3	-289	-3 019	1.8	20.0	118	1 330

For the purpose of the thermodynamic treatment, further molecular constants of clusters $(X_2)_2$ were calculated: force constants (see part B) and barriers to internal rotation V_0 around the central axis of $(X_2)_2$ (difference between the energy of the square and tetrahedron). Calculated molecular constants are summarized in Table II.

B. Vibrational Frequencies

For the calculation of six vibrational modes of clusters $(X_2)_2$, the Wilson FG technique¹⁷ was used. The change of all six edges of the tetrahedron $(X_2)_2$ were chosen as internal coordinates. Length and force constant for the two chemical bonds were taken from the literature for molecule X_2 (ref.¹⁸). Lengths of the four remaining edges were obtained by means of Eq. (3) and for these lengths force constant was calculated:

$$f_r = \left(\frac{\partial^2 E}{\partial r_{ij}^2} \right)_0 \quad (8)$$

Nondiagonal elements of the \mathbf{F} matrix were put equal to zero. With the \mathbf{F} matrix so constructed, the Wilson treatment was carried out. Because of very large difference between the two types of force constants, two modes of six obtained were always identical with the harmonic mode ω of the molecule X_2 , and the remaining four modes (of symmetry B_1, E, A_1) were smaller than ω by several orders of magnitude; the modes are summarized in Table III.

C. Statistical-Thermodynamic Treatment

Thermodynamic characteristics of the reaction studied were calculated by means of standard procedures of statistical thermodynamics based on partition functions¹⁹, which can be easily evaluated from calculated molecular constants.

TABLE III

Calculated Vibrational Frequencies of $(X_2)_2$ Molecules (cm^{-1})
 ω is the harmonic frequency of X_2 molecules¹⁸, 1 and 2 denote parameters 1 and 2; cf. text.

Species	B_1^a		E		A_1		ω
	1	2	1	2	1	2	
$(N_2)_2$	6	10	26	39	35	53	2 358
$(O_2)_2$	7	13	26	43	35	58	1 580
$(Br_2)_2$	4	11	9	27	12	35	321
$(I_2)_2$	3	10	7	23	9	29	215

^a Torsion.

TABLE IV

Comparison Between Calculated and Observed Values of Chemical Thermodynamic Properties (Standard State at 1 atm Pressure)
 Calculated values are presented in two rows. The upper one is based on the complete vibrational partition function; in the lower, the torsional fundamental is replaced by hindered internal rotation.

Species	T, K	ΔH_T^0 , cal. mol ⁻¹		ΔS_T^0 , cal. mol ⁻¹ , deg ⁻¹		ΔG_T^0 , cal. mol ⁻¹		log K_p , K_p in atm ⁻¹					
		exp.	l	2	exp.	l	2	exp.	l	2			
2 N ₂ ⇌ (N ₂) ₂	77	—	-160	-278	—	-7.3	-11.4	—	402	603	0.1-1 ^a	11.9 ^a	3.7 ^a
	77	—	-233	-345	—	-10.4	-13.4	—	569	689	0.1-1 ^a	4.5 ^a	2.1 ^a
2 O ₂ ⇌ (O ₂) ₂	70-83	-269	-133	-384	-15.5	-13.4	-18.4	831	819	918	-2.565	-2.528	-2.832
	70-83	-269	-198	-434	-15.5	-15.9	-19.4	831	926	944	-2.565	-2.856	-2.913
2 Br ₂ ⇌ (Br ₂) ₂	408-15	-2 600	523	-1 289	-15	-7.7	-16.4	3 522	3 680	5 400	-1.886	-1.970	-2.891
	408-15	-2 600	153	-1 421	-15	-10.2	-16.7	3 522	4 312	5 412	-1.886	-2.309	-2.898
2 I ₂ ⇌ (I ₂) ₂	605	-2 900	914	-1 815	-14.4	-7.3	-16.9	5 812	5 356	8 406	-2.094	-1.935	-3.037
	605	-2 900	370	-1 929	-14.4	-9.8	-17.1	5 812	6 301	8 422	-2.094	-2.276	-3.042

^a Degree of association (mol per cent) at 1 atm pressure.

Inasmuch as the minimalization procedure gives only one configuration for clusters $(X_2)_2$, then under the assumption that interactions with other energetic contributions are negligible, interaction energy manifests itself only in the zero point energy term and not in partition functions. The zero point energy, $\Delta E_0^0 = \Delta H_0^0$, was calculated in the following way:

$$\Delta E_0^0 = E_{\text{TOT}} + \frac{1}{2} \sum_i \hbar \nu_i, \quad (9)$$

where the sum runs over the four smallest vibrational modes of cluster $(X_2)_2$.

The thermodynamic treatment was carried out in two ways, differing in their description of the energetic contribution of mutual torsion of subunits X_2 : a) Considering torsion mode in the vibration partition function. b) Omitting torsion mode from the vibration partition function and treating this term by an approximation useful for internal rotation problems²⁰. Experimental and calculated thermodynamic characteristics are presented in Table IV.

DISCUSSION

In empirical calculations of interaction energy, two parameter sets (1 and 2) were used. The first was derived⁹ only for C—C, C—H and H—H interactions, the second for all interactions between H, C, N, O, F, S, Cl, Br and I. In Eq. (7) it has been shown that in the case of parametrization 1, interaction energies between two arbitrary homonuclear molecules are equal. In the case of parametrization 2, different values of interaction energies were obtained. It is seen from Table IV that the differences between results based on parametrizations 1 and 2 are substantial only for heavy atoms Br and I. The parametrization used is not necessarily optimal. However, it was not our purpose, to find parameters giving the best fit with experimental data, but rather to demonstrate the applicability of this procedure.

The values of the dispersion energy given by the two different methods (the method with parametrizations 1 and 2 and the London formula) provide similar values for the O_2 — O_2 and N_2 — N_2 interactions, which is in agreement with results in ref.¹⁵. Significant differences resulted for Br_2 — Br_2 and I_2 — I_2 interactions. Owing to the large value of the bond polarizability of Br_2 and I_2 , the London dispersion energy is much greater than that calculated by the first approximation. Consequently, the total energy is much greater by the monopole-bond polarizability approximation than by the empirical treatment; this is due to the fact that the repulsion energy is described in both procedures in the same or a very similar way. Therefore, we believe that this procedure will prove generally useful only after reparametrization of the repulsion term.

Remarkably enough, the CNDO/2 method gives for the N_2 — N_2 interaction a minimum on the potential-energy curve which possesses reasonable values of both

the intermolecular distance and the depth. We are continuing our study of this and of INDO and MINDO/2 calculations as well as their applicability to F_2 and C_2 molecules.

Our very simple thermodynamic treatment suffers from several shortcomings, the most significant being the assumptions of ideal behaviour, independence of individual energy contributions, and negligible anharmonicity in vibrational modes. In particular, the last two represent, owing to an unusual force field, rather rough approximations. Of the two possible treatments, the one employing the partition function of internal rotation is physically sounder than the one employing a partition function of the torsion fundamental. However it is useful to know that the two treatments give comparable results.

On judging the overall agreement between theoretical and experimental ΔH , ΔS and ΔG values, a treatment making use of the Eliel parameter set and the internal rotation partition function appears to be the most successful. The noteworthy compensation of enthalpy and entropy terms observed in calculations on Br_2 and I_2 using Kitajgorodskij's parameters should be taken as a warning: although ΔH and $T\Delta S$ are greatly overestimated, the values of ΔG are in very good agreement with experiment.

Stogryn and Hirschfelder calculated the mole fraction of the oxygen dimer as a function of temperature by assuming the Lennard-Jones intermolecular potential⁷, obtaining -738 cal/mol for ΔH_{140}^0 . This is slightly lower than the experimental value due to Blickensderfer and Ewing³ ($\Delta H_{140}^0 = -658$ cal/mol), which was obtained from direct spectroscopic evidence for the formation of oxygen dimer in the gas phase.

Nearly fifty years ago Lewis² studied the dimerization of O_2 in liquid N_2 by measuring the magnetic susceptibility. Although the reaction enthalpy was obtained at lower temperature, its value ($\Delta H_{70.8}^0 = -269$ cal/mol) is higher than the above-mentioned one which would mean increasing stability of the dimer with increasing temperature. This discrepancy might be explained by the influence of the different environment in the two experiments.

In the four types of our calculations the reaction enthalpy of oxygen dimerization is always higher than the experimental value of Blickensderfer and Ewing³: the best fit was achieved by means of the Eliel parameters if the torsion fundamental is replaced by internal rotation ($\Delta H_{140}^0 = -381$ cal/mol). In the case of the Lewis data, however, fair agreement is found between calculated and experimental values (Table IV).

REFERENCES

1. Ewing G. E.: Private communication.
2. Lewis G. N.: *J. Am. Chem. Soc.* **46**, 2027 (1924).
3. Blickensderfer R. P., Ewing G. E.: *J. Chem. Phys.* **47**, 331 (1967).
4. Kokovin G. A.: *Ž. Neorgan. Chim.* **10**, 287 (1965).

5. Passchier A. A., Gregory N. W.: *J. Phys. Chem.* **72**, 2697 (1968).
6. Tapia O., Bessis G.: *Theoret. Chim. Acta* **25**, 130 (1972).
7. Stogryn D. E., Hirschfelder J. O.: *J. Chem. Phys.* **31**, 1531 (1959); **33**, 942 (1960).
8. Girardet C., Robert D., Galatry L.: *J. Mol. Struct.* **11**, 305 (1972).
9. Kitaygorodsky A. I.: *Tetrahedron* **14**, 230 (1961).
10. Bondi A.: *J. Phys. Chem.* **68**, 441 (1964).
11. Eliel E. L., Allinger N. L., Angyal S. J., Morrison G. A.: *Conformational Analysis*. Interscience, New York 1965.
12. Huron M. J., Claverie P.: *Chem. Phys. Letters* **4**, 429 (1969).
13. Huron M. J., Claverie P.: *Chem. Phys. Letters* **9**, 194 (1971).
14. Denbigh K. G.: *Trans. Faraday Soc.* **36**, 936 (1940).
15. Mantione M. J., Daudey J. P.: *Chem. Phys. Letters* **6**, 93 (1970).
16. Hanna M. W.: *J. Am. Chem. Soc.* **90**, 285 (1968).
17. Wilson E. B., Decius J. C., Cross P. C.: *Molecular Vibrations*. McGraw-Hill, New York 1955.
18. Shimanouchi T.: *Physical Chemistry an Advanced Treatise* (D. Henderson, Ed.), Vol. IV, Chapter 6. Academic Press, New York 1970.
19. Zahradnik R., Slanina Z., Čársky P.: *This Journal* **39**, 63 (1974).
20. Pitzer K. S., Gwinn W. D.: *J. Chem. Phys.* **10**, 428 (1942).

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