Theoretical Study of the $(Cl_2)_2$ Dimer

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Abstract: Several geometric configurations of the $(Cl_2)_2$ dimer have been studied by quantum chemical methods. Ab initio calculations have been performed, adding the dispersion energy to the SCF supermolecule determination. It is found that the most stable configuration is the L structure, the T and an "open-L" configuration being slightly less stable. The linear geometry is less favorable. This is compatible with the experimental observation of a polar dimer. The relative importance of the different contributions to the intermolecular energy (in particular the charge-transfer energy) and the need for a d polarization function in the calculation of the dispersion energy are discussed. The present results may also be of use for liquid and crystal studies.

I. Introduction

As we noted in a recent paper,[1] little work has been published on the $(Cl_2)_2$ dimer[2-4] compared to the wide range of studies concerning the crystal or liquid chlorine.[5-21] The interest for this dimer has been initiated by the experimental work of Klemperer et al.[2] which concluded the existence of a polar dimer. Two theoretical studies, based on the use of molecular orbitals, have treated this system but, as explained in ref 1, none of them is able to lead to conclusive results. In the first case,[3] the method used is not appropriate to the treatment of such weakly bonded molecules and the values obtained are artificial. In the second study, which chooses the $(F_2)_2$ dimer as a model, practical limitations are involved in the calculations and probably explain the disagreement with the experimental conclusions. The intermolecular potentials used in crystal or liquid studies are not more accurate. Most generally, a simple Lennard–Jones (6,12) potential is still proposed though several authors have shown its inadequacy[8,9,11-13] to predict that the most stable structure of the crystal is the orthorhombic one as known from experiment.[6] Another form of the repulsive interaction has been used[11,18] and other contributions to the intermolecular interactions have also been considered. In particular, the electrostatic quadrupole–quadrupole interaction[12] and the charge-transfer contribution[11] (not taken into account in a (6,12) potential) have been evaluated from semiempirical approximations. It is shown[11,12] that these contributions are not negligible. However, more accurate calculations would be necessary. In this sense, our own calculations on the dimer, obtained from ab initio wave functions, may be useful to crystal or liquid studies in two ways: from a physical point of view, it is interesting to compare the relative stabilities of the configurations in the dimer and in the crystal; from the point of view of the method, a comparison with our results may give information about the possibilities of the semiempirical approximations generally used.

The orthorhombic structure of the crystal[6] is a layer structure. The geometric arrangement of the molecules has been described in many papers:[7-9,11-13,18-20] in a layer the molecules are arranged in rows; two adjacent molecules of different rows have nearly an "open-L" geometry and the shortest distance between two nonbounded atoms is about 3.3 Å.[6,20] For the dimer, no experimental geometry is available. Klemperer et al.[2] suggested that its polar character would be compatible with a T or an L geometry. In the present work, we have studied these two structures. In addition, we have also considered the linear configuration which was surprisingly the most stable geometry in ref 4, and an "open-L" structure, with an angle of 120° between the intramolecular axes, which was the most stable one at the SCF level.[4]

II. Method

Using ab initio wave functions, the dispersion energy is obtained from the perturbation theory and computed according to the scheme described in ref 22. This contribution is added to the SCF supermolecule energy.[23] Such a procedure has been previously used[24] in the case of $(H_2)_2$ and $(Ne)_2$ and takes advantage of the equivalence between the perturbation and supermolecule methods.[25] This is not a rigorous treatment but the main contributions to the intermolecular interactions are then taken into account.

It may be convenient to start the SCF supermolecule calculation with Schmidt-orthogonalized SCF molecular vectors. It is commonly admitted that the difference between the energy of the first iteration performed with such vectors and the SCF energy of the isolated molecules corresponds to the first-order electrostatic and repulsive energy of a perturbation treatment. We checked this equivalency[25] in the case of $(H_2)_2$ and $Li^+ + H_2$. The difference between the SCF energy of the supersystem and the energy of the first iteration (delocalization energy) would correspond to the second-order induction and charge-transfer energy of the perturbation method.

Two expressions of the dispersion energy are proposed in ref 22, corresponding to two different partitions of the molecular Hamiltonian in a double-perturbation scheme. Expressions 1 and 2 of ref 22 are denoted respectively by E'_{disp} and E_{disp} in the present work. When the perturbation series is limited to second order, it seems that E_{disp} gives a better agreement with experiment. However, E'_{disp} are often used in the literature and the results obtained with this expression will also be commented upon in the present paper.

III. Details of the Calculation

As it will be seen in this section, one of the most delicate problems in such calculations is the choice of a good basis set. Some care must be taken, as well for the supermolecule treatment as for the dispersion energy. A very large polarized basis set would be able to correctly describe both contributions but would be very time consuming. If smaller basis sets are used, the characteristics of a reliable basis set are not the same for the supermolecule treatment and for the dispersion energy. Thus, in this case, it can be necessary to use two different basis sets, adapted to the calculation of each contribution. The basis set effect is shown in Tables I and II, for some configurations and some values of the intermolecular distance d. This distance d is chosen as in ref 4: for the L, open-L, and linear configurations d is the distance between the two nearest nonbounded atoms. In the case of the T configuration, d is the distance between the middle of the molecule which is perpendicular to the intermolecular axis and the nearest atom of the molecule lying along this intermolecular axis.

1. Dispersion Energy. For the dispersion energy, it is essential to include diffuse polarization functions. Table I gives the dispersion energy obtained with two different bases: bases I and II. Basis I is an unpolarized basis set: 11 s and 7 p Gaussian

Table I. $(Cl_2)_2$ Dispersion Energy (kcal/mol) at $d = 6$ Bohr Radii (3.175 Å)[a]

	linear configuration		L configuration	
	E_{disp}	E'_{disp}	E_{disp}	E'_{disp}
basis I	−0.88	−0.67	−0.38	−0.29
basis II	−2.49	−1.86	−3.01	−2.26

[a] See definition of d in the text.

Table II. $(Cl_2)_2$ ΔE_{SCF} in kcal/mol

d,[a] Å	linear configuration		T configuration	
	basis III	basis IV	basis III	basis IV
3.175	1.51	2.10		
3.440	0.75	1.10	0.63	0.43
3.704		0.67	0.13	−0.01
3.969	0.25	0.45		
4.233			−0.06	−0.12

[a] See definition of d in the text.

functions, taken from ref 26, are contracted into a "double ζ" set for the valence shells and a minimal set for the inner shells. In basis II, a diffuse d function with exponent 0.22 is added to the previous set. This function is optimized to obtain the largest value of the dispersion energy, as previously done for other systems.[22,24,27] The intramolecular distance has not been optimized. With both bases, we have used the distance of 2.029 Å, obtained in a previous work[28] with a polarized "double-ζ" basis set. This value may be compared with the experimental distance[29] of 1.988 Å. The SCF energies of Cl_2 are respectively −917.709 80 and −917.780 66 au with bases I and II. The polarizability components have been calculated,[30] using basis II. We have obtained respectively[30] 7.94, 3.86, and 5.22 Å^3 for $\alpha_\parallel$, $\alpha_\perp$, and $\bar{\alpha}$. Two experimental determinations[31,32] give $\bar{\alpha}$ = 4.61 Å^3. They give 6.6[31] and 6.33 Å^3 [32] for $\alpha_\parallel$ and 3.62[31] and 3.73 Å^3 [32] for $\alpha_\perp$.

Table I shows that the results obtained with bases I and II differ by a factor of 2.5 for the linear configuration and of 8 for the L geometry. Thus it clearly appears that d functions are important in the linear case and absolutely essential for the L configuration. This means that an unpolarized basis function, as used in ref 4, artificially favors the linear geometry. The reason for this can be understood when we consider the contribution of each molecular orbital: for a molecule lying along the intermolecular axis, the largest contribution to the dispersion energy arises from a σ_g occupied orbital coupled with the first σ_u virtual orbital, while this is no longer the case when the molecule is perpendicular to the intermolecular axis. Thus, when both molecules A and B lie along the intermolecular axis (linear case), 20% of the total dispersion energy (basis II) is due to the molecular orbitals coupling $(\sigma_g)_A(\sigma_u)_A(\sigma_g)_B(\sigma_u)_B$. If molecule B is perpendicular to the intermolecular y axis, such a coupling becomes very small. The largest contribution (4% of the total dispersion energy) is due to $(\sigma_g)_A(\sigma_u)_A(\pi_{yu})_B(d_{x^2-y^2})_B$, followed by $(\sigma_g)_A(\sigma_u)_A(\pi_{yu})_B(\sigma_g)_B$, $(\sigma_g)_A(\sigma_u)_A(\pi_{yg})_B(d_{x^2-y^2})_B$ and $(\sigma_g)_A(\sigma_u)_A(\pi_{xu})_B(d_{xy})_B$. For both geometries, the rest of the dispersion energy is given by a large number of small contributions.

Table I also gives the values of E_{disp} and E'_{disp}. As seen for other systems,[22,33] E_{disp} is systematically larger than E'_{disp}. In the present work, they differ by a factor of about 1.3. Thus, the use of basis I and E'_{disp}, as in ref 4, gives about 27% of the dispersion energy in the case of the linear configuration and only 10% for the L geometry, compared with the use of E_{disp} and basis II.

2. SCF Supermolecule Energy. One of the main sources of error in the supermolecule treatment is due to the well-known "superposition error" which may be large when too small or unbalanced bases are used. Thus, both bases sets described in the previous section would not be good to treat the SCF contribution. Table II gives the results obtained with two bases (bases III and IV) for the linear and the T configurations. Basis III is the "double-ζ" basis set previously used[28] in the treatment of C_2H_4 + Cl_2. The SCF energy of a Cl_2 molecule is −918.8252 hartrees for an optimized intramolecular distance of 2.190 Å. This distance is then used in the SCF supermolecule treatment when basis III is considered. For basis IV, the s and p functions[28,26] are not contracted, and a d function with exponent 0.532 392 is added, optimized in order to obtain the

lowest molecular energy. The SCF energy of Cl_2 is −918.9077 hartrees for an optimized intramolecular distance of 2.011 Å. This distance is used in the SCF supermolecule treatment when basis IV is considered.

Table II allows a comparison between the results obtained with these two bases. ΔE_{SCF} is the difference between the SCF energy of the interacting molecules and the SCF energy of the isolated molecules. We can see that the discrepancy between both series of results is somewhat larger for the linear geometry than for the T one and of opposite sign; as in the previous section, the use of the smaller basis set favors the linear geometry.

It is very difficult to completely eliminate the superposition error. An estimate of this error has been proposed by Boys and Bernardi;[34] they use the dimer basis set instead of the monomer basis set to compute the SCF energy of each Cl_2 molecule (counterpoise method). This method may give an interesting improvement in some cases (see for instance ref 35) but it has also been noted that the correction may be strongly overestimated.[36] An explanation for this last point could be that, in the dimer, the functions of the second molecule are mainly used to describe the second molecule and only partly able to improve the description of the first molecule while, in the counterpoise method, the functions of the second molecule, not required to describe the second molecule, are totally available to improve the description of the first molecule. In the present work, we have used the counterpoise method to estimate the superposition error in the region of the minimum (d = 3.440 Å) for the four configurations. With basis IV we found 0.34, 0.30, 0.25, and 0.13 kcal/mol for the T, L, open-L, and linear configurations, respectively. These values are not very large and, as explained above, probably seriously overestimated. Furthermore, the first three being nearly equal, the superposition error correction should not significantly modify the qualitative conclusions obtained from the uncorrected results. With basis III, the correction is 0.33 and 0.06 kcal/mol for the T and the linear configurations, respectively. We can see that bases III and IV give nearly the same superposition error (as estimated from the counterpoise method) but that basis IV improves the description of the electrostatic and repulsive contributions (Table II). Since it is not possible to obtain a really sure estimate of the superposition error, the results given in the present paper are not corrected. However, the possible effect of this error will be discussed in the text.

The optimization of the molecular geometry may also have a relatively important effect. For instance, in the case of the T configuration, basis III gives ΔE = 0.13 kcal/mol for d = 3.704 Å (Table II). As written above, the molecular distance R is then 2.190 Å. With R = 2.011 Å, the same basis III gives 0.25 kcal/mol.

IV. Results

The study of the basis-set effect presented in the previous section leads us to use basis II for the dispersion energy and basis IV for the supermolecule SCF treatment. Tables III–VI allow an analysis of each intermolecular energy component for the four geometric configurations.

Table III. $(Cl_2)_2$ First-Order Energy in kcal/mol

d, Å	configuration			
	T	L	open L	linear
2.910	6.66 (6.43)[a]	5.84 (6.99)	5.56 (6.45)	
3.175	2.55 (2.52)	2.08 (2.54)	2.06 (2.28)	2.76 (2.26)
3.440	0.94 (1.05)	0.70 (1.01)	0.75 (0.88)	1.43 (0.87)
3.704	0.33 (0.46)	0.21 (0.43)	0.28 (0.36)	0.85 (0.36)
3.969	0.10 (0.21)	0.05 (0.19)	0.12 (0.16)	0.56 (0.16)
4.233	0.02 (0.10)	0.01 (0.09)	0.07 (0.07)	
4.498	0.01 (0.05)			
4.763			0.05	0.23

[a] The values given in parentheses are the repulsive terms of a Lennard-Jones-type potential ($\Sigma_{ij} B/R_{ij}^{12}$) with $B = 2.358 \times 10^6$ kcal mol^{-1} Å^{-12} (ref 13 and 18).

Table IV. $(Cl_2)_2$ E_{ind+CT} in kcal/mol

d, Å	configuration			
	T	L	open L	linear
2.910	−1.61	−2.27	−2.20	
3.175	−0.86	−1.10	−1.06	−0.69
3.440	−0.51	−0.61	−0.59	−0.33
3.704	−0.34	−0.37	−0.36	−0.18
3.969	−0.23	−0.23	−0.23	−0.12
4.233	−0.14	−0.15	−0.15	
4.498	−0.08			

1. SCF Supermolecule Treatment. As explained in section II, it may be interesting to decompose the SCF intermolecular energy, ΔE_{SCF}, into two contributions: the first iteration energy, corresponding to the first-order electrostatic and repulsive energy (ΔE_1) and the delocalization energy, corresponding to the second-order induction and charge-transfer energy (ΔE_{Ind+CT}). We have then $\Delta E_{SCF} = \Delta E_1 + \Delta E_{Ind+CT}$. We shall comment separately these two contributions.

First-Order Energy: ΔE_1. Table III gives the values obtained at the first iteration of an SCF supermolecule treatment. As written in section II, they correspond mainly to the repulsive and electrostatic first-order energies. We can see that all of these values are repulsive. Thus the electrostatic energy, which may be attractive, is not able to compensate the repulsive energy. In the region of the minimum, the most repulsive configuration is the linear one, and the less repulsive one is the L structure.

We have compared our results with some semiempirical determinations of the repulsive energy. Table III gives the values obtained for the repulsive part of a Lennard-Jones-type potential, using the parameters proposed by Ito et al.[13] (which are denoted by "set I" in Table II of ref 18). We see that the agreement is good for the T configuration, less good for the L and the open L ones, and poor for the linear geometry in the region of the minimum (3.175–3.440 Å). This seems compatible with the relative magnitude of the electrostatic contribution: from the expressions given by Buckingham,[37] the electrostatic energy is larger in the case of the linear configuration than in the T one (and of opposite sign). This confirms the hypothesis of Nyburg[12] that it is necessary to take account of the electrostatic contribution. At shorter distances (2.910 Å), the poorer agreement obtained for the L and the "open-L" structures probably means that the description of the repulsive part needs to be improved, as suggested by Hillier and Rice.[11]

The other set of parameters[13] (denoted by "set II" in ref 18) and the Buckingham-type potential proposed in ref 18 give values in poor agreement with our own results.

Delocalization Energy (ΔE_{Ind+CT}) and SCF Energy (ΔE_{SCF}). Since the Cl_2 molecules are not polar, the delocalized energy is mainly due to the charge-transfer energy. Table IV shows that at intermediate distances, this contribution is rather similar for the four configurations, somewhat smaller values occurring in the linear case. However, we must not forget that the superposition error, previously discussed, is included in this delocalization energy. Thus the values of Table IV may need to be somewhat decreased. Following the qualitative trends of the superposition error given by the counterpoise method estimates (section III-2), the T configuration values may become as small as the linear configuration ones, as it is the case at smaller intermolecular distances. Compared to the values of Table III, it is clear that the charge-transfer contribution (even

corrected for the superposition error) is important, in agreement with the semiempirical work of Hillier and Rice.[11] If we add the values of Table III and Table IV, the induction and charge-transfer contribution ensures the stability of the L, "open-L", and T configurations. The most stable one is the L structure, with a minimum depth of −0.18 kcal/mol around $d = 3.969$ Å, then the T configuration with −0.13 kcal/mol, and finally the "open-L" structure with −0.11 kcal/mol for the same intermolecular distance. The correction of the superposition error could give smaller minima and somewhat larger intermolecular distances but would probably not modify the relative order of the stabilities. This relative order of the stabilities is the same as in Table III, not modified by the induction and charge-transfer component. At this SCF level, the linear configuration is still repulsive. This was not the case for the linear $(F_2)_2$ dimer which was attractive in ref 4. We must also note the discrepancy between our results and those of ref 4 concerning the "open-L" configuration: in our calculations, this configuration is less stable than the L-shaped one while it is the contrary in ref 4. Both dimers may have a different behavior. However, the calculations of ref 4 have been performed with a rather small basis set and it would be interesting to see if a larger basis set would modify these relative stabilities.

2. Dispersion Energies: E_{disp}. Table V shows the dispersion energy E_{disp} obtained with basis II. Compared with the values of Tables III and IV, we see that E_{disp} is an important contribution to the stabilization energy of the dimer. This term cannot be neglected as done in ref 3. The largest contributions are obtained for the T and the L configurations which are close together. The open-L and the linear configurations, less attractive, are both similar. We explained in section III-1 the origin of the discrepancy between our results and the values obtained in ref 4. We have not given our values of E'_{disp} in Table V since they are approximately equal to $E_{disp}/1.3$.

The values given in parentheses (Table V) are the attractive term of a Lennard-Jones-type potential, using the parameters proposed by Ito et al.[13] (they are referred to as set I in ref 18, as for the repulsive term). Among the potentials considered in ref 18, set I gives the best agreement with our own values. We can see that this agreement is rather good for the four configurations. This is encouraging for the use of semiempirical determinations of this energy component, at least when the leading term of the multipole expansion is considered. The following term ($C_8 R^{-8}$) may be seriously underestimated in our own determination since no f function is included in the basis set.

3. Total Energy $E_{tot} = \Delta E_{SCF} + E_{disp}$. The total energy (Table VI) is computed as the sum of the SCF energy (ΔE_{SCF}) and the dispersion energy (E_{disp}). We can see that the most stable configuration is the L-shaped one, with a well depth of −2.09 kcal/mol, and then the T and the open-L ones, with −1.69 and −1.67 kcal/mol, respectively, and finally the linear configuration which is much less stable than the other three (−0.51 kcal/mol). As previously discussed, a correction of the superposition error could give smaller minimum depths and slightly larger corresponding intermolecular distances. It would

Table V. $(Cl_2)_2$ Dispersion Energy in kcal/mol (E_{disp})

d, Å	configuration			
	T	L	open L	linear
2.910	-5.06 (-5.39)[a]	-4.71 (-4.96)	-4.09 (-4.15)	
3.175	-3.25 (-3.40)	-3.01 (-3.09)	-2.59 (-2.53)	-2.49 (-2.38)
3.440	-2.11 (-2.21)	-1.95 (-2.01)	-1.67 (-1.61)	-1.61 (-1.50)
3.704	-1.40 (-1.48)	-1.30 (-1.34)		-1.07 (-0.98)
3.969				-0.73 (-0.66)

[a] The values given in parentheses are the attractive terms of a Lennard-Jones-type potential $(-\Sigma_{ij}A/R_{ij}^6)$ with $A = 2196$ kcal mol^{-1} Å^{-6} (ref 13 and 18).

Table VI. $(Cl_2)_2$ $E_{tot} = \Delta E_{SCF} + E_{disp}$ (kcal/mol)

d, Å	configuration			
	T	L	open L	linear
2.910	-0.01	-1.14	-0.72	
3.175	-1.56	-2.02	-1.59	-0.39
	(-1.69)[a]	(-2.09)	(-1.67)	(-0.51)
3.440	-1.68	-1.87	-1.50	-0.51
3.704	-1.28	-1.45		-0.40
3.969				-0.29

[a] The values in parentheses are interpolated. The intermolecular interpolated distances are 3.39, 3.27, 3.28, and 3.45 Å for the T, L, open-L, and linear configurations. Let us note that for the T configuration this distance is not the distance between the two nearest nonbounded atoms.

probably not modify the general conclusions except for the relative order of the stabilities of the T and of the open-L configurations. It is interesting to note that, for the L and the open-L configurations, the distance between the two nearest atoms (3.27 Å) is comparable to the experimental value obtained in the crystal (3.34,[6] 3.32 Å[20]). The use of E'_{disp} instead of E_{disp} gives smaller well depths but the same relative stabilities (-1.38 kcal/mol at 3.38 Å for the L configuration, -1.17 and -1.16 kcal/mol for the T and the open-L structure at $d = 3.52$ and 3.34 Å, respectively, and finally -0.14 kcal/mol at $d = 3.57$ Å for the linear configuration).

The relative stability of the L configuration with respect to the two following ones is very small and could be easily missed with semiempirical calculations. The use of the Lennard-Jones-type potential considered in Tables III and V gives a larger well depth for the T configuration (-1.17 kcal/mol at $d = 3.48$ Å) than for the L configuration (-1.03 kcal/mol at $d = 3.53$ Å), the values for the last two configurations being -0.78 kcal/mol at $d = 3.56$ Å and -0.69 kcal/mol at $d = 3.57$ Å for the "open-L" and the linear case, respectively. This reversal of the stabilities of the T and the L configurations is not due to the dispersion term, as can be seen from Tables III and V. In order to study the effect of the induction and charge-transfer contribution, we have added our own determinations given in Tables III and V, neglecting those of Table IV. We have then obtained an interpolated well depth of -1.20, -1.26, -0.97, and -0.22 kcal/mol at $d = 3.52$, 3.48, 3.37, and 3.69 Å for the T, L, "open-L", and linear configurations, respectively. The energy difference between the T and L configurations becomes very small (both configurations are nearly degenerated) but the relatives stabilities are not modified with respect to Table VI. Thus, the reversal between the stabilities of the L and T geometries is due not only to the charge-transfer contribution but also to the electrostatic contribution and to the description of the repulsive part, as commented by Hillier and Rice[11] and Nyburg.[12] In agreement with the conclusion of ref 11, we also found that the charge-transfer contribution may be very important compared to the total energy. Our study also confirms, as suggested in ref 11, that the dispersion energy (Table V) does not determine the relative stabilities of con-

figurations T and L. It is both the charge-transfer and the first-order contributions which are responsible for this.

V. Conclusions

Taking into account the main contributions to the intermolecular energy, we have shown that the most stable configuration of the $(Cl_2)_2$ dimer has an L structure. However, the T or an "open-L" configurations are only slightly less stable (0.4 kcal/mol) than the L-shaped one. The energy of the linear configuration is much higher than the other three ones. All of these results are compatible with the experimental assumption of a polar dimer.[2]

From a comparison with semiempirical approximations, it appears that the dispersion term is rather easily approximated by a simple formula. However, the situation is less simple for the other terms. A Lennard-Jones-type potential fails to give the right order of the relative stabilities of the configurations, mainly because of the need for the electrostatic and charge-transfer contributions. It is difficult to describe, by a simple expression, this last term which may give an important part of the total energy. These considerations about the possibilities of semiempirical approximations are of special importance since such formulas are generally used in crystal or liquid studies.

References and Notes

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Hydrogenation of Oriented Monolayers of ω-Unsaturated Fatty Acids Supported on Platinum[1]

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Abstract: Oriented monolayers of an ω-unsaturated fatty acid (17-octadecenoic acid, C18:1[17]) have been prepared at the air–water interface and transferred to the surface of clean platinum foils. When the platinum-supported monolayer is exposed to dihydrogen, the olefinic group of the acid is hydrogenated. The rate of this reduction can be varied over a range of 10^4 by changing the pH and metal ion concentration of the aqueous subphase on which the monolayer is prepared and the transfer pressure. The major influence on the rate is the metal ion incorporated into the monolayer: cadmium, an ion considered a catalyst poison, leads to slowly reduced monolayers; magnesium- and calcium-containing monolayers hydrogenate more rapidly; metal ion free monolayers reduce most rapidly. A secondary influence appears to be the rigidity of the film (as estimated by the compressibility of the original monolayer at the air–water interface). The rates of reduction of the supported unsaturated fatty acid monolayers parallel the rates of reduction of 1-pentene vapor on similar monolayer-covered foils. These observations collectively suggest a qualitative picture for fatty acid monolayers supported on platinum as thin, viscous, liquid or liquid-crystalline films. The study of the hydrogenation of supported, unsaturated monolayers provides an unexplored method for the examination of the microscopic structure of these films, and suggests new approaches to the study of mechanisms of heterogeneous hydrogenation.

Introduction

The research described in this paper has examined the hydrogenation of unsaturated fatty acids present as components of oriented monolayer films supported on platinum. This research has two related objectives: (1) *to clarify the structure of oriented fatty acid monolayers on solid supports;* (2) *to explore the usefulness of these monolayers as probes with which to investigate mechanisms of heterogeneous hydrogenation.* Oriented films of fatty acids and derivatives supported on solid substrates have been used previously in studies requiring thin organic films of known thickness or film component geometry; examples include geometrically defined systems for the study of energy transfer[2-4] and photochemical reactions,[5] catalysts for the heterogeneous photochemical cleavage of water,[6] models for biological lipid membrane organization,[7,8] and materials for X-ray diffraction gratings.[9] Although the structures of oriented fatty acid monolayers at the air–water interface are reasonably well defined,[10-12] less is known about the structures of monolayers on solid supports. The physical characteristics which provide the basis for studies of monolayers at air–water interfaces—especially surface pressure–area isotherms and surface potentials—cannot be measured or are poorly defined for thin films supported on solids. Electron microscopy,[7] infrared attenuated total internal reflectance spectroscopy,[13] ellipsometry,[14] and optical spectroscopy[2-4] suggest that *multilayer* films are highly ordered, with the hydrocarbon chains in the all trans-zigzag conformation expected by analogy with the structures of crystalline fatty acids.[13] The inferences drawn from these studies are convincing, but they are derived from observation of sample volumes containing multiple layers and large numbers of molecules, and are pertinent only to the average structure of the multilayer assembly. Detailed information concerning the structure of supported *monolayers* is more difficult to obtain than that of multilayers for three reasons: first, the sensitivity of many of the spectroscopic techniques used with multilayers is too low to be used with a single monolayer; second, monolayers (and also the first layer of multilayer assemblies) seem to be intrinsically more heterogeneous than the outer layers of multilayers; third, the structure of a supported monolayer undoubtedly depends on the composition and morphology of the support surface. Even on smooth, uniform, glass supports, film balance studies,[15] isotopic labeling,[16] and electron microscopy[17] suggest structural heterogeneity; on other supports (platinum,[18] silver,[19] mica[19,20]) the structure of supported films is not well understood.

Despite present uncertainty concerning the structure of oriented, supported organic monolayers, these films appear to have great potential as mechanistic and structural tools with which to study many areas of surface chemistry. Organic monolayer films are materials in which both the molecular composition of the surface and the organization of the groups comprising the surface can, in principle, be controlled. The effective use of oriented monolayers as probes to study the mechanisms of heterogeneous catalysis or cellular adhesion requires that the information extracted about the structure and behavior of the monolayer components be sufficiently detailed at the molecular level to draw mechanistic conclusions. It is not evident that the physical and spectroscopic measurements traditionally applied in studies of oriented monolayers are capable of providing information of the type required for these potential new applications. This paper describes the initial stages of our effort to use the chemical reactions of monolayer