Theoretical Chemistry Comes Alive: Full Partner with Experiment

William A. Goddard III

Summary. During the last decade, advances in computational techniques and in the extraction of chemically useful concepts from electronic wave functions have put theorists into the mainstream of chemistry. Some recent examples of the prediction of spectroscopic quantities and the elucidation of catalytic processes for homogeneous and heterogeneous reactions from theoretical calculations are used to illustrate how theory and experiment are now full partners in chemical research. It is expected that during the next decade the thrust of theoretical chemistry will be to combine the knowledge of fundamental chemical steps and fundamental interactions with advances in chemical dynamics and irreversible statistical mechanics and in computer technology to produce simulations of chemical systems with competing reactions taking place simultaneously at various reaction sites. The promise of such simulation is illustrated by a study of the enzyme thermolysin.

With the invention of quantum mechanics in the 1920's, the foundation was laid for a first-principles explanation for all of chemistry. Starting with the Schrödinger equation,

$$H_e \Psi_i(r_e,R_n) = E_i(R_n) \Psi_i(r_e,R_n) \qquad (1)$$

where e stands for electron; n, nucleus; and i, the ith excited state, one could solve for the wave function Ψ_i, which is the basis for all physical and chemical properties of the system. The ability to solve Eq. 1 did not, however, lead to the demise of experimental chemistry because the solutions are straightforward only for simple systems such as H_2. Even so, approximate solutions of Eq. 1 led pioneers such as Pauling (*1*), Mulliken (2), and others to a conceptual description of bonding that shaped chemistry into its modern form. Until the 1970's, quantitative results from Eq. 1 often disagreed with experimental results. In that era, one could not trust theory (except when it was applied to small molecules such as H_2) unless it was confirmed by experiment, and theorists would generally have been foolhardy to suggest that theory was correct when there was disagreement with experiment. The remarkable change in that situation over the last 15 years will be illustrated with several case histories.

The Coming of Age for Quantitative Quantum Chemistry

Bent versus linear CH_2. The chemically important but very reactive species CH_2 has been a particular challenge for both experiment and theory. In one of the first ab initio (first principles) calculations on a triatomic molecule, Foster and Boys (*3*) in 1960 predicted a bent geometry (128°), but simultaneous spectroscopic studies (*4*) concluded that the molecule is linear. The calculations were considered too crude to be relevant. Everyone believed the molecule to be linear until the increasingly accurate theoretical studies in the late 1960's finally led Bender and Schaefer to insist in 1970 that CH_2 is bent by 135° (*5*). Indirect experimental evidence for such highly bent CH_2 came quickly (*6*), followed by a reinterpretation of the spectroscopic studies (*7*) to confirm the bent geometry predicted by theory. The currently accepted experimental value for the bond angle is 133.84° (*8*).

The singlet-triplet gap in CH_2. Carbon has four valence electrons and four bonding orbitals. Bonding carbon to two hydrogens uses two carbon electrons and two carbon orbitals for the C–H bonds, leaving carbon with two nonbonding electrons and two nonbonding orbitals (denoted σ and π). This results in two low-lying electronic states having very different chemistries, the triplet and singlet states (Fig. 1).

The triplet state is lower in energy, but by how much? Indirect photochemical experiments performed from 1967 to 1971 yielded values for the difference in energy between the singlet and triplet states), ΔE_{ST}, of 2.5 kcal (*9*), 1 to 2 kcal (*10*), and 10 ± 3 kcal (*11*). Early theoretical estimates were usually greater than 20 kcal, but by 1972 a group at Caltech (*12*) obtained $\Delta E_{ST} = 11.5$ kcal using generalized valence bond theory, and a group at University of California, Berkeley (*13*), obtained 13 kcal with an alternative theory, configuration interaction. Although it is difficult to assign error bars to such calculations, the theorists believed that their results were good to ±3 kcal, which was in serious disagreement with some experiments. However, all these experiments were indirect and had serious interpretational uncertainties. Over the next few years, interpretation of the indirect experiments converged on $\Delta E_{ST} = 8 \pm 1$ kcal (*14*), in reasonable agreement with the accepted theoretical value, $\Delta E_{ST} = 11 \pm 3$.

In 1976 this pleasant situation was torn asunder by a "bombshell" from Colorado. Lineberger and his co-workers (*15*) conducted an elegant experiment in which they formed a beam of CH_2^- and used a laser to remove the extra electron. Under these conditions, either the π electron leaves to form singlet CH_2 or the σ electron leaves to form triplet CH_2, so both the singlet and triplet states were observed directly. The experimental results are sketched in Fig. 2. The value for ΔE_{ST} obtained directly from the spectrum, 19.4 kcal, was well outside the range of expected error for either theory or previous (indirect) experiments.

This startling result shattered the complacency of theoretical and experimental chemical physicists. How could everyone be so far wrong? A flurry of experimental and theoretical activity ensued. Theoretical methods had advanced considerably over the years since 1972, and in 1977 a number of extensive calculations were reported (*16*), all indicating ΔE_{ST} to be about 10.4 kcal. New indirect experiments continued to give values around 8 ± 1 kcal (*17*). Consternation and concern reigned for a year or two as these results were appearing. What could be causing the discrepancy?

Finally, in 1978 the Caltech theorists published a paper (*18*) in which they used theoretical results to calculate the energy of vibrational levels, which they then

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used to reinterpret the direct experiments. The result is shown in Fig. 3. The Caltech group claimed that three observed bands (A, B, and C) were hot bands (from vibrationally excited CH_2^- molecules) and that these bands would disappear if CH_2^- were in its true vibrational ground state. This reinterpretation led to an experimental value, ΔE_{ST} = 9.0 kcal (*18*), in reasonable agreement with the best theoretical value (10 kcal) and the best indirect experimental value (8 kcal). The experimentalists were not convinced, but the theorists were, which led the Caltech and Colorado researchers to bet several bottles of expensive French champagne on whether the theorists' interpretation of the experiment was correct. For 3 years the Colorado experimentalists tested this reinterpretation, attempting to find conditions under which the intensities of bands A, B, and C would change. No such evidence was found (*19*) and the bets stood unpaid. Finally, on 29 March 1984, the Colorado group completed the construction of an apparatus that would eliminate the possibility of hot bands, and the first experiment was run with CH_2. Bands A, B, and C disappeared (*20, 21*). The theorists were right! The new direct experiments yielded ΔE_{ST} = 9.0 kcal, and the French champagne began its journey from the University of Colorado to Caltech (*22*).

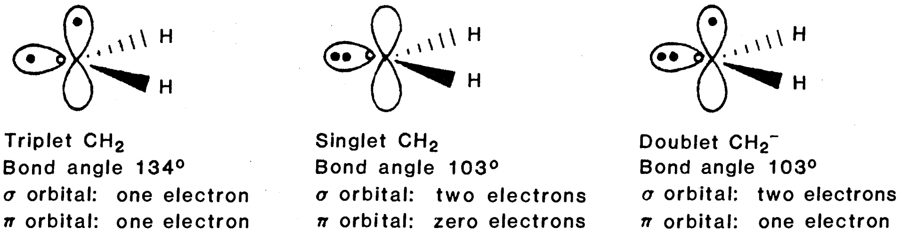


Fig. 1. States of CH_2 and CH_2^-.

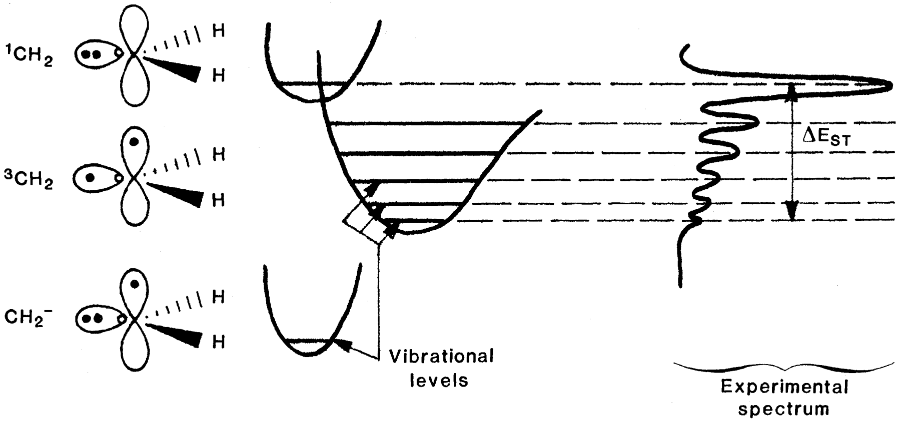


Fig. 2. Photoionization from CH_2^- ($\sigma^2\pi^1$) to yield a singlet state CH_2 ($\sigma^2\pi^0$) with the same geometry results in a large peak in the spectrum. Photoionization to yield a triplet CH_2 ($\sigma^1\pi^1$) leads to a different geometry and hence a number of small peaks corresponding to various vibrational levels of triplet CH_2. The difference between the large peak (singlet state) and the lowest triplet peak yields a direct measure of ΔE_{ST}.

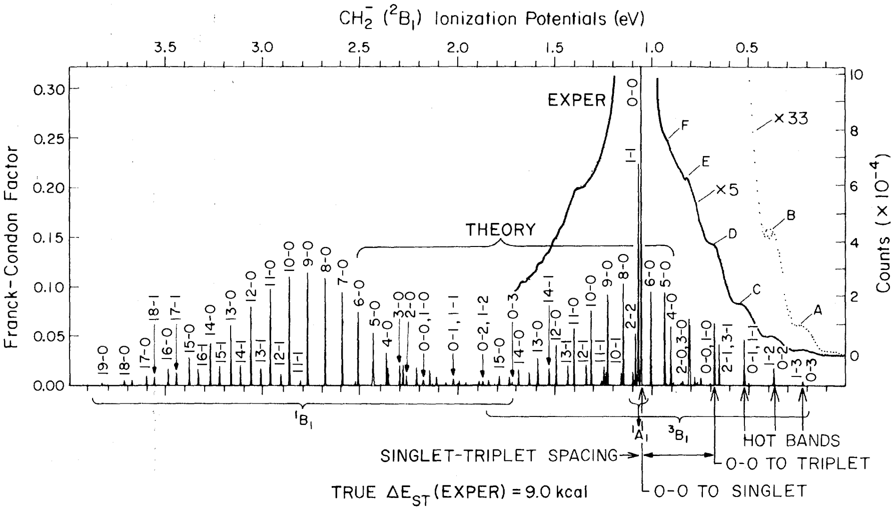


Fig. 3. Predicted photoelectron spectrum (from theory, 1978) and experimental spectrum (1976). From the theory, peaks A, B, and C were assigned as hot bands, with peak D as the 0-0 transition to the triplet state.

Such dramas are continuously being played out as science lurches forward in its efforts to elucidate various phenomena. The new feature here for chemistry was that the theorists were so confident of the accuracy of their results that they hung tough in the face of disagreements with experiment, and then with all-consuming gall they reinterpreted the experiments.

What lies ahead? In the early 1980's, systematic approaches to accurate methods with direct calculations of the first derivatives of the total molecular energy (the forces on the atoms) and the second derivatives of the energy have led to automatic programs for accurate calculation of the geometries and energies of molecules and radicals that can routinely handle systems with up to three or four heavy atoms (for example, carbon) plus hydrogens sprinkled hither and yon (*23, 24*). Indications are that with slight corrections to the ab initio results (*24*), accuracies of ±3 kcal are obtained even for these highly strained species.

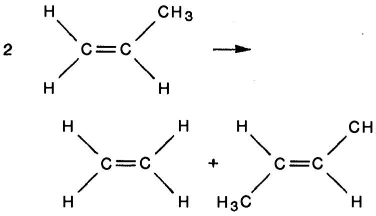
As we approach the mid-1980's, it appears that through use of effective potentials (*25*) to represent the core electrons, comparably accurate results will soon be routine for species containing several heavy atoms such as silicon, germanium, tin, and their neighbors in the periodic table.

Quantitative quantum chemistry has arrived. The theory is now sufficiently accurate that theorists and experimentalists are becoming equal partners in chemical research.

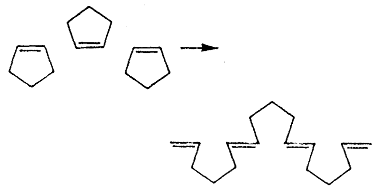
Recent Progress in Qualitative Quantum Chemistry

The above applications illustrate how it is possible to gain quantitatively accurate data from theoretical studies of systems that are hard to study experimentally (reactive intermediates and excited states). This is most valuable but not sufficient. If theory could provide only exact results for any desired property of any system, it would not be any better than a collection of good experiments. What theory uniquely provides is the qualitative principles responsible for the results from a particular experiment or calculation. With proper understanding of the principles, one can predict how new systems will act in advance of either experiment or quantitative calculations. The following case studies illustrate the process.

Olefin metathesis. Several important chemical processes involve olefin metathesis, which is the breaking of carbon-carbon double bonds and the piecing together of the fragments from different molecules to make two new olefins, distinct from the starting materials. For example, the Phillips Triolefin Process (*26, 27*)


(2)

was used until 1973 to convert (then cheap) propylene into butene, which in turn was used to produce butadiene, an important starting material for many chemicals. In a Goodyear process (*26, 27*) cyclic olefins are metathesized to form special polymers.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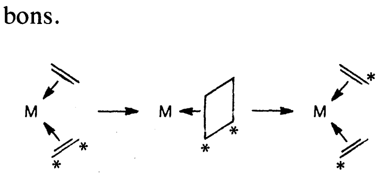
These metathesis reactions do not proceed by themselves; they need a catalyst. Generally, a transition metal compound such as WCl_6 or $MoCl_6$ is used together with a number of additives such as organic aluminum compounds or organic phosphorus compounds. In the early days (up to about 1972), it was thought that the metal served to coordinate two olefins and that this somehow allowed a reaction mixing up the carbons.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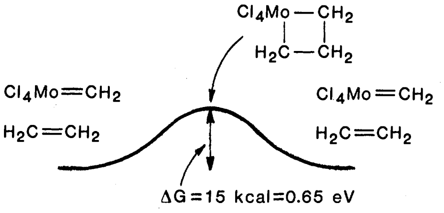
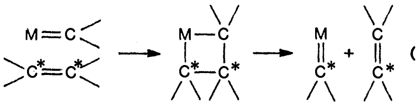


Fig. 4. Free energy along the reaction path (schematic) for metathesis.

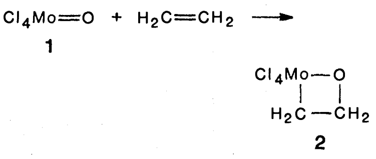
However, a series of ingenious experimental studies (*28*), all indirect, established that the catalytic reactions involve active species having a metal-carbon double bond or a four-membered ring with a metal at one of the corners


(5)

where M = Mo or W. Back in 1970, when the earliest of these studies was published, postulating such species was a bold step since no such species had yet been observed directly. However, researchers later synthesized such species and showed that they are tenable.

In the late 1970's, a group at Caltech initiated a series of studies (*29*) to examine the mechanism of the reaction in Eq. 5. The key intermediate had not yet been characterized experimentally, and there were a number of questions concerning the nature of the metal-carbon bonds in these systems. In addition, no experimental estimates of the energetics were available, so the quantitative results of theory would be valuable. Because good metathesis catalysts are based on tungsten or molybdenum, the group at Caltech examined the process in Eq. 5 and found the results shown in Fig. 4 (*29*). Since metathesis proceeds rapidly at −50°C, they felt that the 15-kcal energy barrier for Eq. 5 was too high to permit that reaction to be in the catalytic sequence. Because this was the first time that first-principles calculations had been performed for such large systems, the theorists at first worried that there might be bad approximations in the calculations. However, several months of tests confirmed their results. Their next thought was that maybe the active catalyst was some other $Mo{=}CH_2$ species. Unfortunately, under catalytic conditions there are a large number of additives present (typically, species such as $Sn(CH_3)_4$ or Cl_2AlCH_3 and PR_3 together with small amounts of alcohol), introducing an enormous number of possibilities, certainly too many to permit calculations for each. What was needed was more insight into how the energetics in Fig. 4 might be controlled by other ligands.

The Caltech group then did what was natural under these circumstances: they dropped the project. Next they started examining how olefins react with metal oxo bonds,



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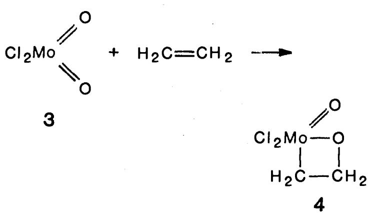


(7)

which led to quite unexpected results. Although the Mo=O bonds in **1** and **3** would be expected to be very similar, the Caltech group found

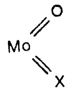
$$\Delta G_{(6)} = +44 \text{ kcal} = +1.9 \text{ eV}$$
$$\Delta G_{(7)} = -21 \text{ kcal} = -0.9 \text{ eV}$$

where $\Delta G_{(\text{Eq. No.})}$ is the change in free energy at room temperature of the corresponding reaction. That is a difference of 65 kcal (2.8 eV) for what would have been expected to be very similar reactions. Obviously something profound must be happening in these systems, and an examination of the wave functions quickly supplied the answer.

The molybdenum-oxygen bonds in the dioxo species **3** are quite covalent, each consisting of a Mo–O σ bond and a M–O π bond, analogous to the C=O bond in formaldehyde ($H_2C{=}O$). Of the six valence electrons on molybdenum, two are involved in the two ionic Mo–Cl bonds, and four participate in the two double bonds to the two oxo groups. Similarly, in the monoxo species **1**, four of the six valence electrons in the molybdenum participate in ionic Mo–Cl bonds, leaving two to bond to the single oxo group. However, there is a surprise with this system. Both of those molybdenum electrons get into $d\pi$ orbitals and make two π bonds to the oxygen. (If the bond axis is z, then one electron is in the xz plane, the other in the yz plane.) Making these two π bonds requires two singly occupied $p\pi$ orbitals on oxygen (p_x and p_y). That leaves two electrons in the oxygen p_z orbital, which overlaps the empty molybdenum d_{z^2} orbital to make a partial σ bond. The end result is a partial triple bond in **1**, much like the bond in carbon monoxide, C≡O; and the M=O bond in **1** is about 30 kcal stronger than those in **3**.

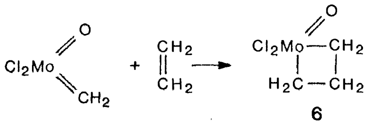
If the molybdenum-oxygen triple bond is so good, why does it not form in the dioxo species **3**? The problem is that if one oxo group in **3** were to make a triple bond, it would utilize both $d\pi$ electrons, leaving nothing for the other oxo group. The compromise is for each to make double bonds. This is analogous to the comparison of O=C=O and C≡O; for CO_2 each oxygen can only make a double bond, whereas in CO, the oxygen can make a partial triple bond.

How do these interpretations explain the 65 kcal difference in energetics for Eqs. 6 and 7? First, in Eq. 6, we must break a stronger Mo=O bond than in Eq. 7, accounting for about 30 kcal of the difference. But what is the origin of the other 30 kcal? To see this, examine product **4** in Eq. 7 more carefully. Of the six valence electrons on the molybdenum, four are used in σ bonds (two to chlorine, one to oxygen, and one to carbon), leaving two electrons to bond to the spectator oxygen (the oxo group that is not changed by the reaction). Thus, in **4** no other ligands except the spectator oxygen can use molybdenum π orbitals; hence, molybdenum can use both $d\pi$ orbitals to make a partial triple bond to the oxygen. It could not do so in the reactant **3**, since the second oxygen also needs to bond to the molybdenum $d\pi$ orbital. Thus, the spectator oxo group changes from having a double bond to having a partial triple bond at the same time that the olefin reacts with the other oxygen. This stabilizes the reaction intermediate by an extra 30 kcal, explaining the observations. These studies led to the following principle: a spectator oxygen adjacent to a ligand X that has a double bond to the molybdenum



promotes reaction at X by stabilizing the resulting intermediate by ~30 kcal.

Immediately, the Caltech group believed that they had the salient clue to the metathesis reaction. Maybe the catalyst was not $Cl_4Mo=CH_2$ but rather the oxo-methylidene (**5**) with its spectator oxo group. With this spectator oxo group they expected the reaction intermediate (**6**) to be stabilized by ~30 kcal and hence for the process in Eq. 8 to be



(8)

5 **6**

exothermic by ~15 kcal. They checked with their computer and found, sure enough, that $\Delta G_{(8)} = -24$ kcal and that, indeed, the spectator oxo had a double bond in **5** and a partial triple bond in **6**.

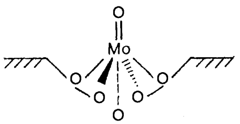
But could this species have been formed in the experimental solutions where catalysis was observed? Indeed, all metathesis experiments involved reaction mixtures containing some source of oxygen (*30, 31*). In fact, Muetterties had shown that rigorous exclusion of oxygen killed the catalyst (*31*).

In a good catalyst, all reaction steps are thermoneutral ($\Delta G \sim 0$). The Caltech group showed that the presence of Lewis acids ($AlCl_3$) or Lewis bases (PR_3), both of which were present in most experimental catalytic systems, would tend to make ΔG for Eq. 8 near zero, leading to the catalytic sequence in Fig. 5. With that, they submitted their papers. Meanwhile, various experimental groups were exploring the chemistry of molybdenum-oxo systems; and simultaneous with publication of the theory, Schrock and his co-workers reported the synthesis of a species like **5** and showed that it undergoes metathesis (*32*). Sometime later, Muetterties and Band carried out a detailed analysis of their metathesis system and provided strong, although indirect, evidence that species **5** is formed and serves as the active catalyst in that system (*33*).

Heterogeneous oxidations. The Caltech group later became interested in some commercially important heterogeneous catalysts responsible for the oxidative dehydrogenation of methanol to formaldehyde (*34*).

$$H_3COH + O_2 \xrightarrow[\substack{MoO_3\\200\text{–}300^\circ C}]{} H_2C{=}O + H_2O \quad (9)$$

Numerous experimental studies of this system had been made, yet there had been no evidence for which sort of surface sites were involved. Since bulk molybdates generally contain MoO_6 (a distorted octahedron) or MoO_4 (a tetrahedron), the theorists believed that the stable surface sites in an oxidative atmosphere would be either **7** or **8**,



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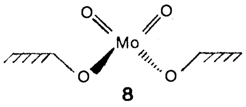

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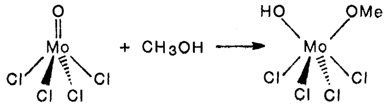
and they proceeded to examine various reaction steps with each. They found, for Eq. 10, $\Delta H_{(10)} = +22$ kcal/mol and $\Delta G_{(10)}$ (25°C) = +33 kcal/mol and, for Eq. 11, $\Delta H_{(11)} = -9$ kcal/mol and $\Delta G_{(11)}$ (25°C) = +2 kcal/mol (*33*); so a surface dioxo unit is required for chemisorption of methanol. (The spectator oxo group is crucial to this stabilization.) To complete the reaction, one C–H bond must be broken. The Caltech group concluded that this requires a second dioxo unit and is favorable only because it is promoted by a spectator oxo group, as shown in Eq. 12 in which $\Delta H_{(12)} = +6$ kcal/mol and $\Delta G_{(12)}$ (300°C) = +6 kcal/mol.



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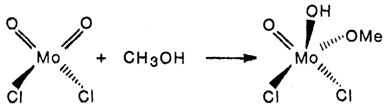

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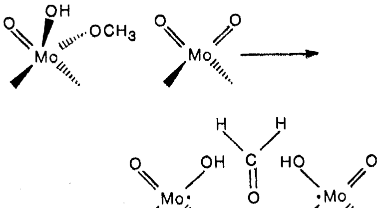


(12)

Thus the theorists concluded that selective oxidative dehydrogenation of CH_3OH to CH_2O requires a dual set of adjacent dioxo units. For each dioxo unit, one of the two oxygens can extract a hydrogen while the other oxygen can provide the spectator oxo stabilization. The spectator-oxo effects are crucial in making the chemisorption, Eq. 11, exothermic and keeping the C–H cleavage, Eq. 12, only slightly endothermic. In this description one would expect Eq. 12 to be the rate-determining step of the process, which has been proved by recent experiments (*34, 36*).

Now the question is, does MoO_3 have a surface with the requisite configuration of adjacent dioxo sites? Indeed, as indicated in Fig. 6, the crystal structure (*37*) of MoO_3 shows that the (010) surface has exactly the configuration needed for the reactions shown in Eqs. 11 and 12, whereas the other low-index faces of MoO_3 do not have the requisite combination of dioxo units. This conclusion that adjacent dioxo units are essential for the catalytic dehydrogenation of CH_3OH is strongly supported by recent experimental studies (*38*). In the presence of O_2, the MoO_3 (010) surface is highly selective for formation of H_2CO and is responsible for nearly all production of H_2CO; the other surfaces give rise to $CH_2(OCH_3)_2$, ether, and very little H_2CO.

The general wisdom had been that the (010) surface of MoO_3 would not be reactive compared with other surfaces because it has no broken chemical bonds (*39*). The theorists' mechanism suggested that this simple reasoning was inade-

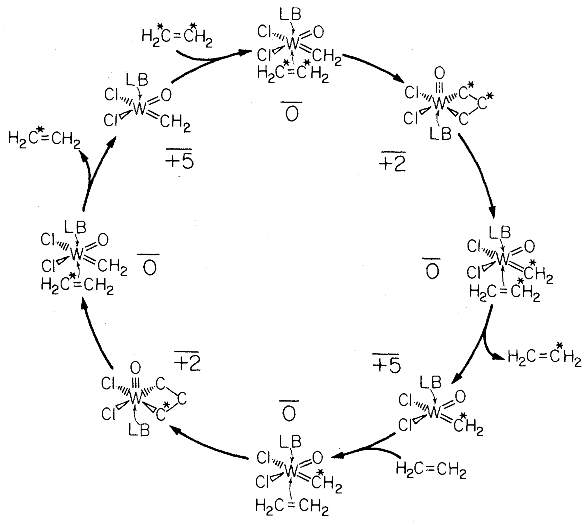
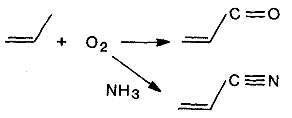


Fig. 5. Catalytic mechanism for metathesis.

quate for MoO_3 (010), and indeed experiments (*38*) have provided strong evidence that MoO_3 (010) is the important surface for formation of H_2CO. It is interesting to note here that exposure of MoO_3 (010) to CH_3OH without O_2 did not lead to reaction (*38, 40*). Presumably, without O_2 the catalyst loses some of its surface oxygen and hence loses the dioxo units required for the chemistry.

The specific mechanism proposed here, involving a dual dioxo catalytic site, is susceptible to many experimental tests. Such interplay between theory and experiment will promote the development of a much more detailed understanding of the fundamental chemical mechanisms of heterogeneous catalytic reactions. Catalytic sites composed of collections of surface dioxo units are also expected to be important in selective oxidation and ammoxidation reactions, Eq. 13 (*41*).



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Summary. Starting with the ideas abstracted from a series of metathesis experiments, theorists found that the theoretical results did not fit the simplest current mechanism and were sidetracked into some parallel studies to develop a better understanding of the basic processes. The result was a new principle, that of spectator oxygen stabilization, which not only provided the missing component in the understanding of metathesis but also provided a framework for understanding a number of other catalytic processes. Indeed, this principle provides a tool that could be useful in designing new catalysts.

One indication of the present state of modern theory is that, when faced with disagreement between theory and experiment, the theorists were sufficiently confident of their results that they continued to examine possible reinterpretations of the experiments until they stumbled onto the key idea. In the mid-1970's, one might have attributed a 20 kcal discrepancy to problems with the theory and gone on to other endeavors, unaware of the existence of any experimental problems. It is also well to emphasize the distinctions between the two aspects of theory being discussed here. First, recent advances in theoretical methods and in the hardware theorists use (high-speed computers cheap enough to belong to individual departments or individual investigators) permit researchers to calculate accurate properties for species that are almost impossible to study experimentally. Although very important, this aspect of theory need not provide new insight. Critical for real advances in chemistry is the second aspect of theory, in which researchers abstract from calculations and experiments the principles and concepts responsible for a particular set of results. With these concepts scientists unfamiliar with the intricacies and pedantics of theory can design materials or catalysts by predicting how the chemistry would be modified by various changes in the metals, ligands, structural environment, and so on. Such concepts allow the scientist to circumvent the numerous tests and experiments traditional to such endeavors.

Onward to Simulation

Is this the end of the story, with theory becoming increasingly able to predict energy surfaces and the detailed sequence of steps in a reaction? No. Even if the energetics for all the possible reaction steps of a catalytic reaction were known, we would still not be satisfied. During the operating lifetime of a real catalyst, its surface is exposed to reactants, reaction intermediates, products, poisons, promoters, and a variety of temperatures and pressures. The ultimate theoretical description of a real system would be to simulate it on a computer. The computer would calculate the motions of molecules and surface atoms as they react, rearrange, migrate, desorb, and so forth, and it would display these motions on a high-speed graphics terminal so that the scientist could change the conditions (temperature, pressure, reactants, surface plane) and visually observe the consequences of those changes. There are a number of formidable problems to solve before this idyllic situation will prevail. Even so, the difficulties seem analogous to those facing quantum chemists 25 years ago.

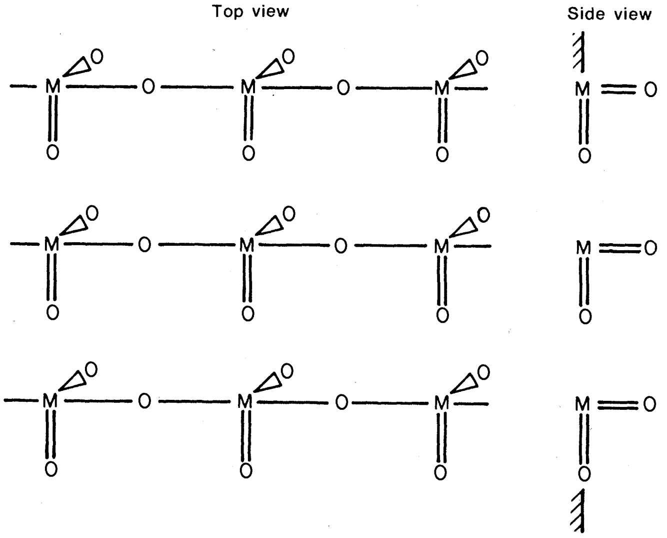

Fig. 6. The (010) surface of MoO_3. The oxygen above the plane lies in the *y* direction and is double-bonded to molybdenum in the plane.

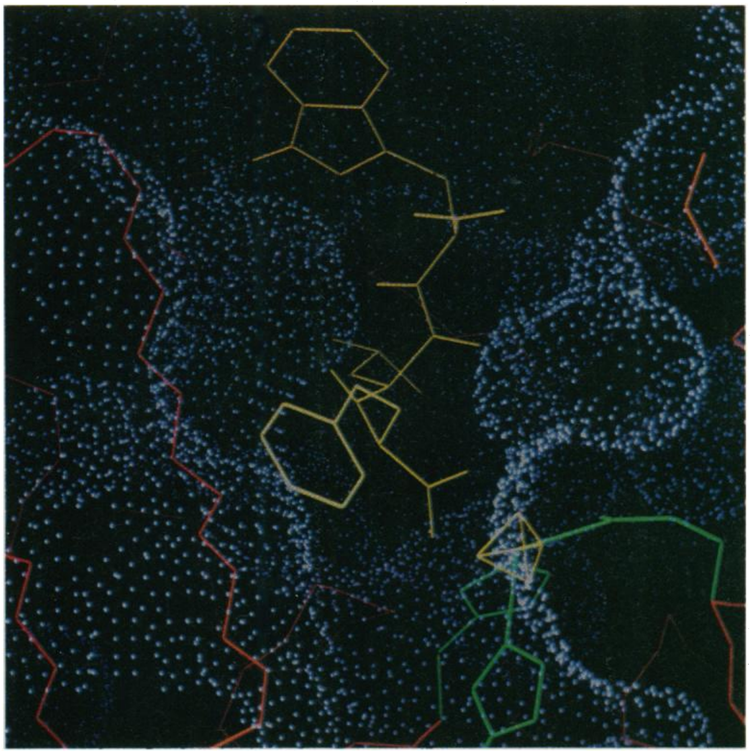

Fig. 7. The solvent-accessible surface for thermolysin. The surface of the enzyme is shown by blue dots. Note the hydrophobic cavity that plays a key role in recognizing substrate or inhibitor.

Some progress in making such simulations has already been made for biological systems, as illustrated by the following example. Thermolysin is a thermophilic (resistant to high temperatures) protease selective for cleaving peptide bonds with hydrophobic residues such as phenylalanine or leucine (*42*). It is also a good model for angiotensin-converting enzyme (ACE) in the sense that good inhibitors for one are good inhibitors for the other (*42, 43*). Indeed, a long-term research program at Merck Sharp & Dohme for the design of inhibitors for thermolysin and ACE recently culminated in a new product that is quite effective in hypertension crises (*43*).

Thermolysin has 2895 atoms (including 443 hydrogens), four calciums, and a zinc). Describing the motions of thermolysin plus a sheath of 170 water molecules by using empirical theoretical force fields and calculating the structure from first principles (*44*) leads to a structure in excellent agreement with experiment (*42*); in fact, the agreement is so good that the differences are not visible in a diagram of the entire molecule suitable for publication. Of course, calculations can also be used to model the enzyme in solution, the biologically relevant situation. Figure 7 shows the surface of the enzyme near the active site and the predicted structure of a new Merck inhibitor (CLT) bound to this site (*45*). In the calculations, the structure of the complete enzyme-inhibitor complex is allowed to relax so that the optimum structure can be calculated. An interesting aspect of this CLT-thermolysin study is that the structure of the complex was predicted without knowledge of experimental structural data, which were being determined simultaneously (*46*). Subsequent comparison of the predicted and experimentally determined structures shows an excellent fit. Theory can, of course, provide much more information than merely the structure of enzyme-inhibitor complexes in solution. The energetics of interaction can be partitioned into components that can be used in designing better inhibitors. In addition, such theoretical studies can be carried out as a function of temperature, providing a model of the dynamics of the system.

Summarizing then, the first point is that theoretical chemistry is coming of age. Theorists are now in a position to tackle many important chemical, biological, and materials problems on an equal footing with experimentalists. The second, and perhaps most important, point is that theoretical chemistry is becoming more and more fun, as the role of theory expands toward the mainstream of nearly all physical, chemical, and biological phenomena relevant to society. The ability of theory, at last, to contribute substantially to the elucidation of interesting catalytic processes bodes well for the future. A new age is approaching in which theory and experiment working together will sort out the most intimate details of catalytic processes and translate the data into a conceptual form that other chemists and engineers can use to design new processes.

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