Infrared Photochemistry (I): Laser-Catalyzed Reactions

Photochemistry has traditionally required visible or ultraviolet light. High-power infrared lasers may soon change this situation, however, and researchers forecast a possible laser revolution in preparative and synthetic chemistry.

Already chemists have used infrared lasers to drive—at room temperature—reactions that normally require high temperatures. Chemists have selectively enhanced one from among many possible pathways that may occur in thermally driven reactions. And they have created compounds that are difficult to synthesize by ordinary methods. All in all, laser infrared photochemistry holds great promise for the synthesis of many chemical products that would otherwise be difficult to achieve. Production of nuclear reactor fuel enriched in uranium-235 is just one such example.

Two features of lasers, their monochromaticity and their high intensity, have made infrared photochemistry possible in the last few years. Moreover, infrared lasers, especially the carbon dioxide laser which emits light at numerous discrete wavelengths in the region from 9.2 to 11.0 micrometers, are generally the highest powered lasers available. And, according to a recent National Science Foundation report,* the cost per photon of a CO_2 laser can be about a hundred times less than that of the visible argon ion laser, thus making the use of infrared lasers relatively attractive for large-scale commercial processes.

Infrared photochemistry occurs when the light absorbed by an assembly of molecules produces a nonequilibrium distribution of occupied rotational and vibrational states which then selectively influence the course of a chemical reaction in some way that can be clearly differentiated from a thermal effect. The monochromaticity of laser light guarantees that only the molecular species which have molecular energy levels precisely matching the laser's frequency can be photoexcited even when molecules differ only by containing different isotopes of the same element.

Since many reactions, especially endothermic ones, have large activation energies, absorption of a single laser photon, in itself, is not enough to drive a reaction, but can only cause rotational and vibrational transitions within the ground electronic state. Thus, in many of the reported instances of laser-catalyzed reactions, each molecule actually absorbs several infrared photons. Multiple photon absorption, as the process is called, has become possible only because of the high intensities achievable with lasers.

At Cornell University, for example, Simon Bauer and his associates have investigated the role of CO_2 laser irradiation on decomposition reactions of the type $2AB \rightarrow A_2 + 2B$, in part because they thought that laser-induced heating effects and true photochemical processes could be clearly distinguished in these cases. In order to obtain conditions for multiple absorption of infrared photons, the researchers placed the reaction cell within the optical cavity of a CO_2 laser, where gaseous samples were subjected to an intensity of about 150 watts per square centimeter. And in order to minimize collisions between molecules, which can deexcite molecules between steps in the sequential absorption process, they relied on quite low gas pressures of 5 millitorr or less (1 torr = 133 pascals).

For the reaction $2D_3BPF_3 \rightarrow B_2D_6 + 2PF_3$, Bauer and K.-R. Chien concluded that the decomposition proceeded by the sequential absorption of three photons, each having an energy of 2.8 kilocalories per mole, which had the effect of reducing the apparent activation energy of the reaction from 29.3 to 3.5 kcal/mole. However, the physical meaning of an activation energy is not obvious when the reactants are in nonequilibrium distributions of quantum states.

Absorbing Many Photons

At pressures higher than the millitorr level, collisions become much more likely, and the energy deposited in a particular vibrational mode of a molecule does not remain localized in that mode. Instead, the energy is rapidly converted, by the collisions, into translational energy (the V-T process, for collisional deexcitation from vibrational to translational energy). The net effect is a rise in the temperature of the gas. The V-T process is even faster in liquids than in gases, where the speed of the conversion depends on the gas pressure.

A way to overcome this problem is by irradiating with such an intense laser that the absorbing molecules reach a state of high excitation before any collisions can occur. A collisionless multiple photon absorption process, in which only the molecules containing the desired isotope are selectively driven all the way to dissociation by the laser, is the basis for much excitement and competition among investigators working on isotope separation right now. Applications of multiple photon infrared photodissociation (the name given to this process) to isotope enrichment will be discussed in a subsequent article.

Avigdor Ronn of Brooklyn College of the City University of New York has studied multiple photon absorption processes in methyl halides. Ronn uses a high-power, pulsed CO_2 laser that, when focused, provides up to 10^8 watts per square centimeter to drive reactions between the methyl halides and molecular chlorine. Such reactions do not proceed at a measurable rate at room temperature.

For the reaction of methyl fluoride, which strongly absorbs CO_2 laser light, and chlorine, Ronn measured infrared and mass spectra of the contents of the reaction cell before and after irradiating with the laser. Ronn found that he could produce, depending on the chlorine pressure, CH_2FCl, $CHFCl_2$, or $CFCl_3$ together with HCl in concentrations about 20 times greater than those of CH_3Cl and FCl, in agreement with the thermodynamically expected reaction probabilities. He was not able to unequivocally resolve the pathway for these chlorination reactions, however.

Similar results have been obtained by Walter Braun and Wing Tsang at the National Bureau of Standards, Gaithersburg, Maryland. These investigators used a focused, pulsed CO_2 laser to photolyze alkyl halides. In most cases, the photolysis proceeded by the elimination of a hydrogen halide—that is, by the thermodynamically lowest energy and hence preferred channel. Braun and others believe, however, that, if the laser intensity is sufficiently high, it may be possible to excite molecules to such high levels that new reaction channels are reached and products not normally observed are generated. This could happen if the lowest energy channel required a geometrical rearrangement of the molecule that took longer to effect than the time between absorption events, for example.

Other researchers have done experiments in multiple photon absorption photochemistry based on the observation that molecules excited into specified vibrational states may preferentially produce only some reaction products from among all those possible. At the Los

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The Laser Revolution in Energy-Related Chemistry, available from the Energy-Related General Research Program Office, National Science Foundation, Washington, D.C. 20550.

Alamos Scientific Laboratory Steven Rockwood and J. W. Hudson used a CO_2 laser to drive the reaction $H_2 + BCl_3 \rightarrow HBCl_2 + HCl$. In the usual thermal process, several other products, in addition to $HBCl_2$ and HCl, result.

Karl Kompa of the Max Planck Institute for Plasma Physics, Garching, West Germany, and his co-workers at the Institute for Inorganic Chemistry of the University of Munich, have used CO_2 laser irradiation to synthesize icosaborane ($B_{20}H_{16}$) from diborane (B_2H_6), whereas conventional pyrolysis of diborane results in a mixture of compounds, none of which is icosaborane. And at the National Bureau of Standards, Joseph Ritter and Samuel Freund (now at Los Alamos) obtained evidence that irradiation of CF_2Cl_2 (Freon 12) with a CO_2 laser resulted in difluorocarbene ($:CF_2$), as an intermediate product. This highly reactive radical may be useful in various chemical synthesis processes.

In all the above-mentioned experiments researchers found that the enhancement of selected reactions due to absorption of laser light was extremely sensitive to the frequency of the laser; that is, the frequency had to match, or nearly match, a resonant frequency of the molecule. Some researchers have also found that they can selectively induce different reactions, depending on the frequency of the laser. For example, Kompa and his co-workers studied the series of reactions:

$$B(CH_3)_3 + HBr \rightarrow B(CH_3)_2Br + CH_4$$
$$B(CH_3)_2Br + HBr \rightarrow BCH_3Br_2 + CH_4$$
$$BCH_3Br_2 + HBr \rightarrow BBr_3 + CH_4$$

The researchers found they could enhance the rates of the first and third by tuning the laser frequency to 970.5 cm^{-1} ($1\ cm^{-1} = 3 \times 10^{10}$ hertz), whereas they drove the second and third by adjusting the frequency to 1039.4 cm^{-1}.

It is possible to demonstrate selective enhancement of chemical reactions even in cases where excitation of specific vibrational modes should be rapidly redistributed by collisions. At the University of Southern Illinois, Carbondale, Robert Zitter and Donald Koster studied the effect of irradiating CF_2ClCF_2Cl (Freon 114) with a low-power continuous wave (CW) CO_2 laser at two different frequencies. These investigators found that the rate of decomposition was about 160 times faster at 921 cm^{-1} than at 1052 cm^{-1}. The result is puzzling because at the low intensity (25 watts per square centimeter) and high pressure (300 torr) of the experiment there should be about 10^4 molecular collisions between each

MIT Patents IR Laser Photochemistry

On 2 March 1976, U.S. Patent 3,941,670 was granted to George W. Pratt, Jr., of the Massachusetts Institute of Technology (MIT), Cambridge. Researchers in the now-burgeoning field of infrared laser photochemistry (see accompanying story) were either dismayed or amused when they learned that the patent appeared to cover virtually all foreseeable applications of photochemistry involving infrared lasers.[*]

The genesis of Pratt's claim was in the mid-1960's when investigators were eagerly exploring the properties of the carbon dioxide laser, which emits in the infrared between about 9 and 11 micrometers. Pratt, who is an electrical engineer, says that while most investigators were looking for ways to expand the wavelength range of these high-power lasers by trying different molecules as the lasing medium or by altering the isotopic composition of the molecules, the idea came to him to reverse the process and use the laser to selectively excite certain chemical or biological molecules.

Pratt demonstrated his idea most thoroughly in experiments in which he used a carbon dioxide laser to sterilize various substrates painted with the heat-resistant spores of *Bacillus subtilis*. Analysis showed that only about 1 in 10^5 spores survived laser irradiation, provided that the laser frequency was one strongly absorbed by the spores. This is the origin of the selective excitation component of the claim.

But the name of the game in the patent business is that, once having demonstrated a new process, the inventor and his attorneys attempt to identify the basic concepts involved and look for other places to apply them. Thus, the patent application begins with specific results but becomes successively broader and more general as the claim's reach expands, often to cover as much territory as the patent examiner will allow. While agreeing with this proposition, Pratt emphasizes his belief that the concept of selective excitation and alteration of chemical and biological activity by irradiation with an infrared laser was in fact novel at the time the patent was filed in 1970 and that a thorough search of the literature uncovered no body of prior knowledge.

Probably the statement "the patent examiner made a mistake" adequately, if undramatically, summarizes researchers' reaction to the patent. Criticism focuses on its breadth and its lack of specific teaching outside of the sterilization application. Laser isotope separation patents, for example, list specific laser frequencies and identify particular molecular energy levels used in the process being patented. The critics also assert that selective excitation of vibrational and rotational modes by infrared laser was a well-known principle, even if it was not an already established item in the literature of the late 1960's.

The patent, which is assigned to MIT, should have an impact primarily on companies hoping to find commercial applications for infrared photochemistry with lasers. Production of enriched uranium for nuclear reactor fuel is the currently most talked about scheme of this type, but many others are possible. Pratt emphasizes that there is absolutely no intent to inhibit basic research in infrared photochemistry, but that MIT greatly desires to license rights to developers of commercial processes. A number of organizations have already been contacted by the university for just this purpose.

Most likely, no challenge will come to the patent until a company large enough to shoulder the financial burden of litigation comes along with a viable laser chemistry process, although observers seem to be nearly unanimously of the mind that the patent could not withstand such a test. But for this expectation, some researchers would be scratching their heads and wondering why they did not try for a patent themselves.—A.L.R.

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[*] One of the broader claims of the patent covers "A method of altering the biological or the chemical activity of molecular species by irradiation, that comprises, generating laser radiation at a frequency which selectively excites vibrational and rotational states of the irradiated species, directing said laser radiation upon the molecular species, said laser radiation being adjusted to lie in the range from about 350 cm^{-1} to about 3,500 cm^{-1}, and controlling the frequency and at least one of the intensity and the time duration of the laser radiation to cause said altering of the biological or the chemical activity selectively to occur and to selectively control the level of said activity. . . ."

photon absorption event. Since both frequencies were strongly absorbed by the Freon, it seems that collisional redistribution of the energy by way of the V-T process, which would remove the frequency selectivity, did not occur.

Zitter speculates that a collisional process may be occurring in which a collision between two molecules transfers vibrational energy from one molecule to the other, raising the latter to a higher energy state. At high laser intensities, there are few unexcited molecules in a gas because the laser excites so many of them as soon as they reach a low energy state. Thus, there is a good chance that molecules already in a highly energetic state can become further excited by the collisions and eventually driven into dissociation, somewhat as in multiple photon absorption. This well known collisional phenomenon, called the V-V process, for vibrational-vibrational energy transfer, can compete with V-T processes when the energy levels of the colliding molecules nearly match, because the energy transfer would then be a resonant transfer. Experiments are now under way to determine if this or some other phenomenon is, in fact, involved.

Laser Heating Effects

Ultimately, in commercial chemical synthesis, it may be desirable to work at both high pressures (50 to 100 torr) and high intensities (10^6 watts per square centimeter) in order to obtain economically viable production rates, argues Ernest Grunwald of Brandeis University. Under such conditions, collisions should efficiently redistribute all the selectively absorbed vibrational energy in a few nanoseconds, according to extensive studies by George Flynn of Columbia University, Bradley Moore of the University of California at Berkeley, and others.

Yet, in experiments with laser-induced decomposition of HCClF, CCl_3F, and $CClF_3$, Grunwald, Kenneth Olszyna, and David Dever (of Macon Junior College, Georgia) find results that must be interpreted as if all the vibrational energy remains locked into the mode excited by the CO_2 laser for the duration of its 0.3-microsecond pulse. Their conclusion follows because the amount of reaction obtained per laser pulse was different from that which would have been seen if the equivalent amount of energy was distributed among reactant states in a statistical or thermal way. There is as yet no model for how this locking effect can come about, however, and some chemists are skeptical of this interpretation.

The source of the skepticism derives in part from numerous reports in the literature of apparently nonthermal distributions of product molecules (some species produced more and others less than expected) after laser irradiation. Laser excitation can, however, be simultaneously responsible for thermal enhancement of reaction rates and nonthermal product distributions. In these situations, the laser is just an expensive Bunsen burner, albeit one with certain exciting possibilities.

For example, at Cornell, Bauer and Walter Shaub have shown that controlled temperatures from 500° to 1500°K can be obtained in a few milliseconds in a gas irradiated with a CO_2 laser. In their experiments, Bauer and Shaub used a CW laser having an output intensity of about 10 watts per square centimeter to irradiate a gas mixture containing various organic molecules and sulfur hexafluoride at pressures from 10 to 100 torr. The sulfur hexafluoride absorbs the laser light, and collisions transfer the energy to the ambient gas, heating it rapidly. In this way, the researchers were able to "flash thermolyze"—that is, thermally decompose—the organic molecules in reaction times of only a few seconds.

Because the heat derives from the laser light, the temperature is highest where it is absorbed in the center of the reaction cell, not at the cell walls. Therefore, inhomogeneous surface reactions do not occur, and the distribution of products varies somewhat from that of the usual thermally produced reaction.

Since the energy of a vibrational quantum is so much less than the energy needed to break many chemical bonds, a natural question for chemists has been: Exactly what is the effect of vibrational excitation of reagents on a chemical reaction? The simplest explanation would be that the activation energy of the reaction is reduced by the energy of the vibration. Such a view is far too naive, however, as many experiments in recent years have shown.

The most notable of these involve highly exothermic reactions in which the energy released ultimately appears as heat. But chemiluminescence (fluorescence emitted by product molecules in excited electronic or vibrational states) measurements of the products in the time before collisions redistribute the energy or in molecular beams experiments show clearly that the excess energy goes preferentially into only a few of the available electronic and vibrational states. Chemists then argue that, by the principle of microscopic reversibility, the reverse endothermic reaction must be preferentially driven only when energy is directly injected into those same states. Thus, all energy is not equivalent insofar as driving a reaction is concerned, and the effect of vibrational excitation must be more complex than a simple reduction of an energy barrier.

One way of looking at the role of vibrational excitation in reaction rates called information theoretic analysis, has been developed by Richard Bernstein of the University of Texas at Austin and Raphael Levine of the Hebrew University, Jerusalem, Israel. As applied to endothermic reactions, the method is based on an analysis of the deviation between the rate which is actually observed and that which would be expected if all molecules of the same total energy (but distributed differently over the accessible quantum states and translational motion) reacted at the same rate.

Vibrations Not Always Effective

Previously, Bernstein, Levine, and Avi Ben-Shaul of the Hebrew University had shown that a logarithmic measure of this deviation, termed the surprisal, was in many cases a linear function of the vibrational or rotational energy. Thus, this technique provides an easy way of analyzing experimental or theoretical data to extract the specific contributions of different modes of excitation.

Recently, Levine and Jörn Manz of the Technical University of Munich, analyzed several endothermic reactions in this way and concluded that vibrational excitation of reagents can be more effective in enhancing reaction rates than can be accounted for by the added energy alone, especially when low-energy vibrational states are excited. But, as the molecule's internal energy approaches the free energy of the reaction, vibrational excitation is increasingly ineffective. Being essentially a means for analyzing data, however, information theoretic analysis cannot explain the origin of these phenomena.

The role of vibrational excitation of ozone on the slightly exothermic reaction $NO + O_3 \rightarrow NO_2 + O_2$ has been extensively investigated, in part because the energy of a CO_2 laser photon is comparable to the activation energy of the thermally driven reaction. Hence, if an effect exists, as it does, it ought to be easily measurable.

At room temperature, whether the ozone is in an excited vibrational state or not, the nitrogen dioxide is produced in both electronically and vibrationally excited states, the concentrations of which can be monitored by visible and infrared chemiluminescence, respectively. In addition, ozone that is vibrationally excited

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can relax to the ground vibrational state by way of the V-T process. Thus, in order to determine in detail the effect of laser excitation on the reaction rate, the rates of five separate reactions must be differentiated. Such a complete analysis is yet to be accomplished.

Early experiments were performed by separate groups at the Naval Research Laboratory, Washington, D.C., consisting of Robert Gordon (now at the University of Illinois at Chicago Circle) and Ming Chen Lin, and at the National Bureau of Standards, consisting of Michael Kurylo, Andrew Kaldor (now at the Exxon Research and Engineering Company, Linden, New Jersey), Braun, and their associates. Although their data were not precisely in agreement, the two groups found that laser enhancement seemed to be about equally effective in producing both electronically excited and vibrationally excited nitrogen dioxide and that, overall, the reaction was enhanced by about a factor of 10.

Most recently, experiments over a wide range of temperatures by Gordon, Jerry Moy, and Ezra Bar-Ziv at the Chicago Circle campus led to the conclusion that about 43 percent of the vibrational energy in ozone was contributing to the reduction in the activation energy for the reaction yielding electronically excited nitrogen dioxide. Similar results have yet to be obtained for the reaction leading to vibrationally excited nitrogen dioxide.

Finally, Terrill Cool and Kin-Kwok Hui at Cornell have separately measured (at room temperature) the visible and infrared components of the chemiluminescence from the product nitrogen dioxide. They were able to determine that, not only does the laser excitation enhance both reactions, but that it preferentially enhances the production of electronically excited nitrogen dioxide as compared to vibrationally excited nitrogen dioxide by a ratio of 2 to 1. This result updates the earliest experiments, in which it was not possible to completely separate the contributions of each component to the overall reaction, and is also in agreement with the information theoretic analysis assertion that vibrational excitation is less and less effective for increasingly exothermic reactions.

In modern molecular dynamics, theorists calculate reaction rates from the trajectories of reactants and products over multidimensional surfaces (hypersurfaces) that represent the potential energy of the chemical system as a function of the relative positions of each molecule. The effect of vibrational excitation on a reaction rate, then, must be described in terms of changing these trajectories, and the different effects of different modes of excitation must be related to the details of these surfaces.

To test these ideas, some years ago, John Polanyi and Wing Hing Wong of the University of Toronto made trajectory calculations for a variety of model surfaces—that is, surfaces not related to any real chemical system. Polanyi and Wong found that, for simple exchange reactions of the type $AB + C \rightarrow A + BC$, increasing the translational energy of the reactants was most effective in enhancing the reaction rate when the energy barrier separating the reactants and products was at a maximum early in the collision—that is, as the reactants are still approaching one another. Vibrational excitation, on the other hand, was most effective when the energy barrier came late in the collision, as the products begin to separate.

In another study, Polanyi and Man Hung Mok discovered that predominantly exothermic reactions tend to have early barriers, whereas largely endothermic reactions tend to have late barriers. Philip Brooks and his associates at Rice University have experimentally confirmed these conclusions, at least in part, in their molecular beam experiments on the reaction $K + HCl \rightarrow H + KCl$. They found that laser excitation of the hydrogen chloride to its first vibrational state enhanced the reaction rate 100-fold. But increasing the translational energy by about the amount equivalent to the vibrational excitation had only 10 percent of this effect on the slightly endothermic (2 kcal/mole) reaction.

Thus, the trajectory calculation approach to molecular dynamics provides a measure of support for the empirically found correlations between the type of reaction and the effect of vibrational excitation or reaction rate. While this augurs well for the future of infrared photochemistry with lasers, researchers caution that the accumulation of much more basic photochemical data on a wide variety of compounds and the development of inexpensive, tunable, high-power lasers are both necessary before very many commercial-scale processes will be possible. At present, for example, in addition to the CO_2 laser, the only high-power infrared lasers for photochemistry include the carbon monoxide and hydrogen fluoride lasers, which emit light at wavelengths near 5 micrometers and 2.7 micrometers, respectively.

—Arthur L. Robinson