Chem. Soc. Rev., 1990, **19**, 407–437

Infrared Laser Powered Homogeneous Pyrolysis

By Douglas K. Russell
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LEICESTER, LEICESTER
LE1 7RH

1 Introduction

Infrared molecular lasers, capable of very high output power, were discovered over a quarter of a century ago. Almost immediately, the potential of these lasers in the initiation and study of chemical reactions, particularly in the gas phase, was recognized. Early experiments were motivated by the possibility of the promotion of selective reaction arising from the very specific nature of the excitation process. It was also hoped that the narrow band excitation provided by laser sources could be used in the efficient separation of isotopes. While these aims have in part been realized, it soon became clear that infrared lasers had the potential for considerably wider application in kinetic and mechanistic investigations. In particular, the need for a chance coincidence between laser output and absorption in the target molecule could be eliminated by use of a chemically inert IR absorber. In this method, energy is absorbed in a vibrational mode of the photosensitizer, and rapidly converted into heat (translational energy) *via* efficient relaxation processes. Energy is then transferred to the reagent molecule *via* collisions in much the same manner as in conventional pyrolysis, and this process is therefore known as *Infrared Laser Powered Homogeneous Pyrolysis*, or IR LPHP.

The major advantage conferred by this technique, in comparison with conventional methods, is implied in the term 'homogeneous'. Since energy is conveyed directly into the gas, then initiation of reaction is unambiguously homogeneous. In practice, most experiments are carried out under conditions where cell walls remain cool, and thus secondary wall processes are also largely eliminated. This can lead to a great simplification in disentangling the contributions of homogeneous and heterogeneous processes in complex systems; this is especially so in cases where deposition occurs, and the surface thus produced acts as an auto-catalyst for primary or subsequent processes. On the other hand, the generation of an inherently non-uniform temperature brings its own problems, especially in the extraction of meaningful kinetic parameters from observed rates.

In the next section of this Review I shall trace the development of the IR LPHP technique from the early, essentially qualitative, studies, to the sophisticated pulsed methods now used in the determination of reaction parameters. There follow descriptions of the major experimental components, and of some pertinent validation investigations and theoretical considerations. The final section consists of three case studies of areas where the IR LPHP technique has found useful application, including some drawn from my own laboratory. It is intended that this Review should be introductory rather than in-depth in its approach, and illustrative rather than comprehensive in its coverage. If I have under-represented some aspects of the topic I can therefore only offer my apologies, and assure readers that no judgement of relative significance is thereby implied.

A. Note on Nomenclature and Scope.—The interaction of infrared laser radiation with molecules in the gas phase is a vast subject, and has been the subject of an enormous number of investigations over the past 25 years. Clearly, there have been many objectives behind these efforts, and it is therefore appropriate at this stage to delineate the scope of this Review, and to introduce some terminology.

The investigation of the absorption of IR laser radiation by molecules forms, of course, part of the subject of *IR Spectroscopy*. The study of the fate of absorbed energy, initially deposited into a single vibrational (and also sometimes a single rotational) level, at powers below that required for any chemical action we can class as *IR Laser Photophysics*. Such studies would include, for example, the rates and selection rules for energy transfer between vibrational, rotational, and translational degrees of freedom. If the energy deposited is sufficient to cause specific chemical action within the absorbing molecule, we may consider this to be *IR Laser Photochemistry*: because several IR photons are usually required to overcome the activation barrier in a single molecule, this may also be known as *IR Laser Multiple Photon Dissociation*, or IR LMPD. The eventual fate of the absorbed IR energy is its distribution over all degrees of freedom in the system, including translation (heat). Under the right circumstances, the temperature rise thus produced may be sufficient to induce thermal chemical reaction, either in the absorber or in added reagents. This process, known as *IR Laser Powered Pyrolysis* (IR LPP) or *IR Laser Induced Pyrolysis* (IR LIP), must be carefully distinguished (both conceptually and experimentally) from the direct photochemical effect described above. The situation is slightly confused by the common usage of the word 'photosensitizer' to describe the IR absorbing species; although 'energy transfer agent' or even 'energy conversion agent' would perhaps be more accurate, I shall use the term sanctioned by convention. Finally, we add the term 'homogeneous' to yield *IR Laser Powered Homogeneous Pyrolysis* (IR LPHP) to distinguish this process from those where gas phase reaction is induced through laser heating of a surface, as is used in the process of laser writing (or pantography). It is the features and advantages peculiar to the LR LPHP technique which I shall discuss here, although the neighbouring areas described above clearly provide us with essential information.

2 Historical Background

The first molecular laser operating in the infrared region of the electromagnetic spectrum was the carbon dioxide laser, discovered in 1964 by Patel and co-workers.[1] This was rapidly followed by developments which led to the operation

---

[1] C K N Patel, W L Faust, and R A McFarlane, *Bull Am Phys Soc*, 1964, **9**, 500

of the laser at high power.[2] This laser operates on transitions between the $v_3 = 1$ vibrational level and the $v_1 = 1$ and the $v_2 = 2$ vibrational levels of CO_2 (*i.e.*, the $3^1_0\,1^0_1$ and $3^1_0\,2^0_2$ transitions). Population inversion of these levels is efficiently achieved in an electric discharge by near-resonant energy transfer from vibrationally excited nitrogen molecules to the $v_3 = 1$ antisymmetric stretching vibration of CO_2. Laser emission may be realized over a range of vibration–rotation components of these vibrational transitions near 10.6 μm amd 9.6 μm. These components are conventionally described in the form '10P(22)' for the $J = 22$ component of the P-branch of the 10.6 μm band.

The first use of IR lasers in inducing chemical reaction seems to have been that of Bordé and co-workers.[3] These workers observed that ammonia at pressures of a few torr (1 torr = 1 mmHg = 133.3 N m^{-2}) emitted a yellow luminescence on irradiation with the 10P(20) line of the CO_2 laser at powers above 40W. Spectroscopic analysis of this luminescence showed that the emitter was the $NH^{\cdot}_2$ free radical. By using a pulsed CO_2 laser, they were able to measure a decay rate for the light emitted by the radical. These observations they attributed to the near resonance of rotational components of the 2^1_0 vibrational transition in NH_3 with the CO_2 laser output, and IR LMPD of the NH_2–H bond. At the pressures used, it is more likely that it was IR LPHP that was actually observed. This work was followed in 1967 by similar observations on a range of hydrocarbons.[4] In this case, various aromatic hydrocarbons were produced from ethene, propene, or allene. Although the above work represents the first experimental observations, a number of workers, principally Russian, had suggested the possibility earlier, and had considered some theoretical aspects.[5]

As mentioned above, one of the motivations behind early work on IR laser induced reactions arose from the hope that the excitation of specific vibrational modes in molecules might lead to control of the course of reaction, and in particular might open the way to efficient separation of isotopes. The first demonstration of this latter phenomenon was reported by Mayer *et al.*[6] These workers subjected a mixture of CH_3OH, CD_3OD, and Br_2 to the output of a HF chemical laser, and observed depletion of the CH_3OH at the expense of the CD_3OD. This was attributed to selective excitation of the OH bond, relative to the OD bond. Doubt has since been cast on the interpretation of these results, which may have been due to a simple kinetic isotope effect. The first genuine laser isotope separation was reported in 1974 by the group of Letokhov,[7] who

---

[2] G. Moeller and J. D. Rigden, *Appl. Phys. Lett.*, 1965, **7**, 274; C. K. N. Patel, P. K. Tien, and J. H. McFee, *ibid.*, 290.

[3] C. Bordé, A. Henry, and L. Henry, *Compt. Rend. Acad. Sci. Paris, Ser. B*, 1966, **262**, 1389.

[4] C. Cohen, C. Bordé, and L. Henry, *Compt. Rend. Acad. Sci. Paris, Ser. B*, 1967, **265**, 267.

[5] F. V. Bunkhin, R. V. Karapetyan, and A. M. Prokhorov, *Sov. Phys. JETP, 1965*, **20**, 145; G. A. Askar'yan, *ibid.*, 1965, **21**, 439.

[6] S. W. Mayer, M. A. Kwok, R. W. F. Gross, and D. J. Spencer, *Appl. Phys. Lett.*, 1970, **17**, 516.

[7] R. V. Ambartzumian, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, *Sov. Phys. JETP Lett.*, 1974, **20**, 273; R. V. Ambartzumian, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, *ibid.*, 1975, **21**, 171.

achieved a 1.6-fold enrichment of $^{11}B:^{10}B$ by exposing mixtures of BCl_3 and D_2S to the 10R(30) line of a pulsed CO_2 laser.

We now turn to the photosensitized IR LPHP process, which forms the central theme of this Review. In 1972, Tardieu de Maleissye suggested that the pyrolysis of saturated hydrocarbons or alkynes (neither of which absorbs CO_2 laser radiation directly) could be achieved by exposing a mixture of the gas and SF_6 to laser radiation;[8] shortly afterwards, he and co-workers demonstrated this experimentally for both ethyne and ethane.[9] The end products in this case were a fine powder of carbon (which rapidly occluded the entrance window, and prevented further reaction) and presumably hydrogen.

This technique was developed to a state of considerable sophistication in an extensive investigation reported in 1975 by Shaub and Bauer.[10] Among other achievements, these workers demonstrated the range of temperatures achievable and established suitable experimental regimes of pressure, laser power, and time of exposure; in addition, they demonstrated the possibility of using a reference 'chemical thermometer' technique for the measurement of the kinetic parameters of a series of reagents. This work established the credentials of IR LPHP as a viable and quantitative technique of considerable versatility, and it is highly recommended to the interested reader as an introduction to this Review.

Since 1975, work using IR LPHP on both the development and application fronts has been extensive. As will become apparent shortly, one of the principal impediments to accurate quantitative work arises from the generation of a non-uniform temperature profile in the laser-induced pyrolysis. This has been elegantly circumvented in a number of developments using pulsed laser sources, principally by the group at SRI in California.[11] Of other workers who have made significant contributions, we must mention the very extensive work of the group of Pola in Prague[12] on the application front, and the investigative studies of Zitter and Koster at Southern Illinois University.[13] The topic has formed a more or less significant part of a number of reviews since 1970, and some of these are given as references 14–20. The interested reader is also referred to the proceedings of two Conferences held in Czechoslovakia in 1986 and 1989, which were wholly or partially devoted to the topic of IR LPHP.[21,22]

---

[8] J Tardieu de Maleissye, *Compt Rend Acad Sci Paris, Ser C*, 1972, **275**, 989

[9] J Tardieu de Maleissye, F Lempereur, and C Marsal, *Compt Rend Acad Sci Paris, Ser C*, 1972, **275**, 1153, F Lempereur, C Marsal, and J Tardieu de Maleissye, *ibid*, 1974, **279**, 433

[10] W M Shaub and S H Bauer, *Int J Chem Kinet*, 1975, **7**, 509

[11] G P Smith, P W Fairchild, J B Jeffries, and D R Crosley, *J Phys Chem*, 1985, **89**, 1269

[12] J Pola, *Spectrochim Acta, Part A*, 1990, **46**, 607

[13] R N Zitter, *Spectrochim Acta, Part A*, 1987, **43**, 245

[14] C B Moore, *Annu Rev Phys Chem*, 1971, **22**, 387

[15] N K Karlov, *Appl Optics*, 1974, **13**, 301

[16] J T Knudtson and E M Eyring, *Annu Rev Phys Chem*, 1974, **25**, 255

[17] S Kimel and S Speiser, *Chem Rev*, 1977, **77**, 437

[18] V S Letokhov, *Annu Rev Phys Chem*, 1977, **28**, 133

[19] W C Danen and J C Jang, in 'Laser Induced Chemical Processes', ed J I Steinfeld, Plenum, New York, 1981

[20] K L Kompa and J Wanner, 'Laser Applications in Chemistry', Plenum, New York, 1984

[21] 'Chemistry by IR Lasers', *Spectrochim Acta, Part A*, 1987, **43**, 129—300

[22] 'Laser Induced Chemistry', *Spectrochim Acta, Part A*, 1990, **46**, 441—669

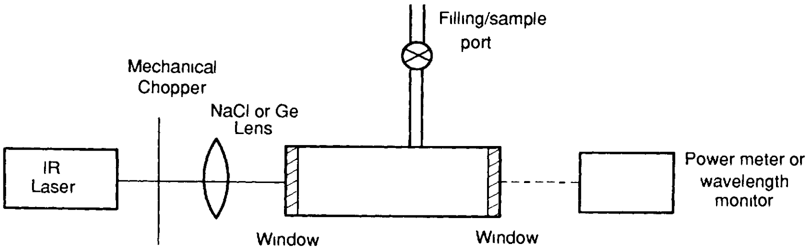

Figure 1 *Schematic diagram of the basic elements of the IR LPHP technique. Not shown are arrangements for monitoring cell contents*

3 Experimental Considerations

In this section, I shall consider the requirements of the equipment used in IR LPHP experiments. Of course, precise experimental arrangements have been very varied, depending on the nature of the investigation. However, some elements are common to all studies, and I shall describe variations and sophistications within the framework of the very simple setup illustrated in Figure 1.

In this arrangement, the reagent gas or gases, mixed with a photosensitizer if required, are contained in a static cell. The cell is fitted with suitable ports for filling and sampling as required, and one or two windows of appropriate material. The cell is exposed to the output of an IR laser, whose characteristics are monitored in an appropriate manner. Changes in the chemical composition of the cell contents are monitored by one of a number of methods. Other parameters of the cell and its contents (pressure, some measure of temperature, *etc.*) may also be monitored. I shall now consider some of the components of Figure 1 in more detail.

A. Pyrolysis Cells.—The most popular design for static pyrolysis cells is the Pyrex or metal cylinder, fitted with windows for axial irradiation, as indicated in Figure 1. For investigations related to the importance of convective motion in the cell, it may be mounted either horizontally or vertically. Typically, such cells are quite small—in our own experiments, for example, the cell has a length of 7—10 cm and an outside diameter of 3.8 cm, giving an overall gas volume of 50—100 cm^3; many are much smaller. The advantage of this is that at the pressures used (a few torr), very small quantities of material are used (a few μmol), and this permits the study of scarce or expensive compounds. Moreover, the small dimensions aid the rapid establishment of a steady state temperature distribution in the cell, and also the rapid redistribution of reactants and products (see below). The cell is fitted with ports as appropriate—at least a filling port, and access for such techniques as gas chromatography, nuclear magnetic resonance spectroscopy, or mass spectrometry.

For other purposes, specialized cells have been designed. Some workers have added a buffer volume to maintain pressures at or near the room temperature value In the pulsed experiments of Smith *et al*,[11, 23] a shorter and wider toroidal cell is employed to ensure a more uniform absorption of laser radiation in the irradiated reaction zone than in that described above, this is further aided by replacing the rear window by a mirror In addition, in these investigations the gas mixture flows slowly through the cell In their investigations of the effects of convection on reaction rates, Shaub and Bauer used a multi-compartment cell which could be irradiated either horizontally or vertically[10] For large scale mechanistic and synthetic studies, Bristow *et al* have used a mechanically pumped circulating cell, which proved capable of preparations on the 100 mg scale[24] For temperature studies, cells fitted with thermocouples have been designed[25, 26] Krasa *et al* have used a NaCl box for IR thermoluminescence studies of temperature distributions[27]

B. Window Materials.—The primary requirements for a suitable window material are that it be highly transparent to the laser radiation (usually CO$_2$ laser radiation near 10 µm), that it possess adequate mechanical strength and thermal stability, and that it be chemically inert These factors, allied to economic considerations, have naturally established NaCl and KCl as favourite materials[10] However, these do suffer from some disadvantages The generation of 'hot spots', caused either by uneven multimode laser power profiles or absorption by solids deposited on windows, can easily lead to thermal stress and unpredictable fracture along cleavage planes[24] Another problem of particular importance in our own work lies in the hygroscopic nature of the alkali halides, even minute traces of adsorbed water can quite radically alter the course of reaction in moisture-sensitive organometallic compounds Both of these problems are avoided by use of ZnSe windows, which has lower absorption at 10 µm, lower thermal expansion, and higher thermal conductivity,[28] on the other hand, its high refractive index does require that such windows be provided with anti-reflection coatings Despite its higher cost, its greater durability leads to a considerably enhanced useful life

C. Infrared Lasers.—As described in the Introduction above, the CO$_2$ laser is almost universally used in IR LPHP experiments Apart from its high power capabilities, it is relatively cheap, robust, and simple to operate In its most familiar low pressure mode of operation, this laser is capable of continuous wave output powers of up to several kW in beams of a few cm^2 area at about 200 discrete wavenumbers ranging from 900 to 1100 cm^{-1},[29] typically, however, more

[23] D F McMillen, K E Lewis, G P Smith, and D M Golden, *J Phys Chem*, 1982, **86**, 709, also K E Lewis, D F McMillen, and D M Golden, *J Phys Chem*, 1980, **84**, 226

[24] N J Bristow, B D Moore, M Poliakoff, G J Ryott, and J J Turner, *J Organomet Chem*, 1984, **260**, 181

[25] P Kubat and J Pola, *Collect Czech Chem Comm*, 1948, **49**, 1354

[26] W P Horn, M S Sheldon, and P C T de Boer, *J Phys Chem*, 1986, **90**, 2541

[27] J Krasa, P Engst, and M Horak, *Spectrochim Acta Part A*, 1990, **46**, 559

[28] Manufacturers, Catalogue, Specac Ltd, 1989

[29] K Narahari Rao and A W Mantz, in 'Molecular Spectroscopy Modern Research', ed K N Rao and C W Mathews, Academic Press, 1972, New York

modest powers of up to 100W are normally used in LPHP applications. For reproducible quantitative work, it is advisable to use a laser provided with both frequency and power stabilization. By pressure broadening the laser emissions in a transversely excited atmospheric pressure (TEA) CO_2 laser, frequency coverage over the working range can be made quasi-continuous.[30] Low frequency modulation of the laser putput may be accomplished either by a mechanical chopper (up to a few kHz) or by electric modulation of the resonant laser cavity length using a mirror mounted on a piezoelectric stack. For faster time-resolved applications, it is necessary to produce short, powerful, and reproducible pulses. By using the technique of Q-switching, it is possible to produce pulses of a few J in times of a few ns (*i.e.* instantaneous powers in the GW range). A review of recent technical developments and requirements in this area of relevance to IR LPHP has been provided by Quack *et al.*[31] In all applications, it is sometimes necessary to focus the laser beam into the pyrolysis cell; this is usually accomplished using NaCl or Ge optics, or front reflecting mirrors at very high powers. The wavelength and power characteristics of the laser output are readily monitored in continuous wave experiments using commercial monochromators and thermal power meters. Where necessary, the power profile of the laser beam can be visualized using standard thermoluminescent plates, or measured using techniques such as traversing a slit or pinhole across the beam profile.[32] For pulsed measurements, the fast rise times of photon drag or pyroelectric detectors are required, together with the appropriate electronic signal processing.

Of other lasers in the mid-IR region, chemical lasers based on vibration–rotation transitions in HF and HCl have found some application, especially in the study of the dynamics of these species themselves. Since they both have output in the 3 μm region, they have both also been used in the direct excitation of O–H bonds.[6]

D. Monitoring of Reaction.—Once again, the choice of method for monitoring the composition of the cell contents is largely dictated by the aims of the particular investigation. For gross compositional changes on a long (>1 second) time scale, any standard analytical technique may be used. In their original work, Shaub and Bauer used gas chromatography with flame-ionization detection,[10] and variants of this method have also been used in subsequent studies.[33,34] On the other hand, the majority of current workers have favoured non-invasive spectroscopic techniques, notably IR spectroscopy.[35–37] This is particularly

---

[30] A. J. Beaulieu, *Appl. Phys. Lett.*, 1970, **16**, 504; A. K. Laflamme, *Rev. Sci. Instrum.*, 1970, **41**, 1578.

[31] M. Quack, C. Ruede, and G. Seyfang, *Spectrochim. Acta, Part A*, 1990, **46**, 523.

[32] R. N. Zitter, D. F. Koster, A. Cantoni, and J. Pleil, *Chem. Phys.*, 1980, **46**, 107.

[33] H. Pazendeh, C. Marsal, F. Lempereur, and J. Tardieu de Maleissye, *Int. J. Chem. Kinet.*, 1979, **11**, 595.

[34] K. A. Holbrook, G. A. Oldershaw, and M. Matthews, *Int. J. Chem. Kinet.*, 1985, **17**, 1275.

[35] K. Dathe, P. Engst, J. Pola, and M. Horak, *Collect. Czech. Chem. Comm.*, 1980, **45**, 1910.

[36] W. Fuss, G. Mengxiong, K. L. Kompa, and Z. Linyang, *Spectrochim. Acta, Part A*, 1987, **43**, 193.

[37] A. Watanabe, Y. Koga, K. Sugawara, H. Takeo, K. Fukuda, C. Matsumura, and P. M. Keehn, *Spectrochim. Acta, Part A*, 1990, **46**, 463.

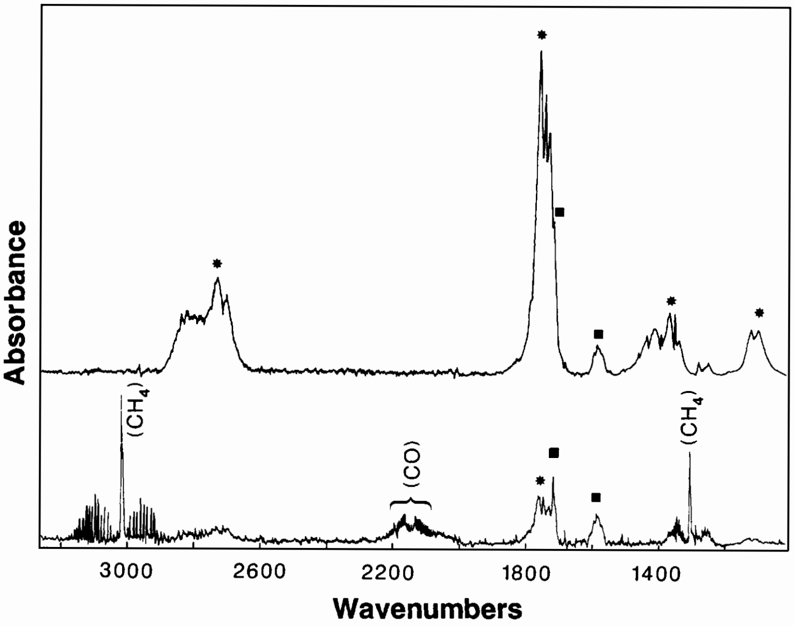

Figure 2 *FTIR spectra of a mixture of* SF_6 *and* CH_3CHO *before (above) and after (below) exposure to* CO_2 *laser radiation Features not identified on the Figure are due to* SF_6 (■) *and* CH_3CHO (✱)

convenient, since one may examine the cell contents *via* either the irradiation windows or an additional pair mounted crosswise for *in situ* monitoring This is the method used in our own work,[38] the well-known additional advantages conferred by Fourier transform IR spectroscopy, such as the speed of data acquisition and the ease of spectrum manipulation, are even more evident in this application Figure 2 shows 'before' and 'after' FTIR spectra in a typical IR LPHP experiment Other workers have used mass spectrometry [39]

For monitoring on a shorter time scale, particularly in pulsed experiments, faster methods are obviously needed For example, in their study of the reaction of OH radicals with hydrocarbons, Smith *et al* monitored OH concentrations using Laser Induced Fluorescence,[11] and this method is also the most widely used in IR LMPD studies Other workers have exploited the rapid scan and high sensitivity and resolution capabilities of tunable lead salt semi-conductor diode IR lasers to monitor changes in rotational and vibrational levels,[40] and others

---

[38] G A Atiya, A S Grady, S A Jackson, N Parker, and D K Russell, *J Organomet Chem* 1989 **378** 307

[39] F W Lampe and J Biedzycki, *Spectrochim Acta, Part A*, 1990, **46**, 631

[40] K Sugawara, T Nakanaga, H Takeo, and C Matsumura, *Chem Phys* 1989 **135** 301

have used techniques such as simple or resonance enhanced multiple-photon ionization.[41,42]

It is pertinent under this heading to raise an issue to which we shall return in more detail below. As already pointed out, the IR LPHP technique generates a non-uniform temperature profile in the pyrolysis cell, with a maximum near the cell axis, and the cell walls remaining at close to room temperature. Under these conditions, of course, reaction rates are highly non-uniform, with the bulk of reaction effectively occurring in a relatively small volume around the temperature maximum; some workers have called this the 'active' volume. Unless sophistications are introduced to account for this (as in many of the pulsed experiments[11,23]), monitoring techniques such as those described above can measure only bulk (*i.e.*, cell-averaged) reaction rates, and the extraction of meaningful kinetic parameters is apparently not possible. However, as shown below, this may not actually be the case: indeed, the observation of cell-averaged concentrations may well be the most straightforward way of obtaining such parameters. To this end, we have investigated the possibility of using the acoustic resonance frequency of the cell and its contents as an *in situ* method for monitoring the average concentration in the cell during pyrolysis.[43] This is also described more fully below.

E. Photosensitizers.—The ideal photosensitizer is characterized by the following features:

(i) very strong absorption of radiation at wavelengths emitted by the laser;
(ii) very rapid intra-molecular vibration–vibration and vibration–rotation/translation energy conversion, and very efficient intermolecular energy transfer;
(iii) high thermal stability;
(iv) chemical inertness;
(v) low thermal conductivity.

Just as the most widely used laser is the CO_2 laser, by far the most popular photosensitizer is SF_6. This molecule has an extremely high absorption for a number of lines in the CO_2 laser spectrum, reaching a maximum of 1.8×10^7 mol^{-1} cm^2 (at room temperature) for the 10P(16) line near 948 cm^{-1}.[44] Neglecting the effects of bleaching and temperature dependence, this leads to an absorption of $>99.5\%$ of incident laser light over a path of 5 mm at the normal working pressure of 10 torr. Partly because of this strong absorption, and partly because of its importance in IR LPHP, SF_6 has been the subject of many studies of state-to-state energy transfer, both in power regimes where dissociation occurs

---

[41] D. M. Rayner and P. A. Hackett, *J. Chem. Phys.*, 1983, **79**, 5414.
[42] G. P. Smith, personal communication.
[43] G. A. Atiya and D. K. Russell, unpublished work; G. A. Atiya, Ph.D. Thesis, University of Leicester, 1990.
[44] A. V. Nowak and J. L. Lyman, *J. Quant. Spectrosc. Radiat. Transfer*, 1975, **15**, 945.

and below this threshold.[45] Recent measurements using a pulsed TEA CO_2 laser and infrared diode laser measurements of CO/SF_6 mixtures have shown that the vibrational energy absorbed by the SF_6 is transferred to translation and rotation with a relaxation time of 10 μs torr.[40] Thus, at the usual working pressures, IR laser radiation absorbed by SF_6 appears as heat in the system within 1 μs. The chemical stability of SF_6 is very familiar as an elementary example of the relative influence of kinetic and thermodynamic factors: the SF_5–F bond dissociation enthalpy (at 389 kJ mol^{-1}) is actually lower than that of some competing photosensitizers (*e.g.* SiF_4 at 594 kJ mol^{-1}) but reactions involving SF_6 are rarely observed under the normal working conditions. Exceptions to this comes from our own work on organoaluminium species,[38] and that of Pola *et al.* on CH_3SiCl_3;[46] these observations are quite consistent with the known exceptional strengths of the Al–F and Si–F bonds.[47] Thermally, SF_6 is stable well above 1200K.[48] The final point concerning thermal conductivity has received less attention than the others described above. SF_6 is a notoriously poor thermal conductor: indeed, it is widely used as a gaseous insulator.[49] This permits the generation of highly inhomogeneous temperature profiles at comparatively modest laser power input. Indeed, in some studies inert gases are added precisely to flatten out this profile (*e.g.*, ref. 50). However, as we shall see below, this may actually detract from one of the major advantages of the IR LPHP technique.

Of other photosensitizers, only SiF_4 has found widespread use;[51] one example where it has particular value is in the study of PH_3, with which SF_6 reacts.[52] Although it is thermally as stable as SF_6, it is a somewhat poorer IR absorber and is fairly reactive towards, for example, water. Other workers have used C_6F_6[53] or NH_3.[54]

4 Investigative and Validation Experiments and Theoretical Considerations

Not surprisingly, the experimental complexity of the IR LPHP technique has engendered a considerable number of theoretical investigations of aspects such as the absorption of the IR laser radiation, the rate of appearance of this energy as heat, the temperature, diffusion, and convection characteristics of the heated gas mixture, the mechanistic interpretation of observed reactions, and the deduction of reaction rate parameters. Many of these considerations have been coupled with experimental investigations designed to test the validity of the conclusions drawn; in this section I shall follow this lead.

---

[45] M Dubs, D Harradine, E Schweitzer, J I Steinfeld, and C Patterson, *J Chem Phys*, 1982, **77**, 3824

[46] J Pola, J M Bellama, and V Chvalovsky, *Collect Czech Chem Comm*, 1981, **46**, 3088

[47] Handbook of Chemistry and Physics (60th Edition), ed R C Weast, Chemical Rubber Co Press, Boca Raton, 1980

[48] J L Lyman, *J Chem Phys*, 1977, **67**, 1868

[49] 'Physical Properties of Inorganic Compounds', ed A L Horvath, 1975, Arnold, London

[50] J Pola, M Farkacova, and P Kubat, *J Chem Soc*, *Faraday Trans 1*, 1984, **80**, 1499

[51] W Tsang, J A Walker, and W Braun, *J Phys Chem*, 1982, **86**, 719

[52] J Blazejowski and F W Lampe, *Spectrochim Acta, Part A*, 1990, **46**, 627

[53] N Selamoglu and C Steel, *J Phys Chem*, 1983, **87**, 1133

[54] C Steel, V Starov, R Leo, P John, and R G Harrison, *Chem Phys Lett*, 1979, **62**, 121

A. Photosensitizer Absorption Spectroscopy.—Partly as a consequence of the popularity of the CO_2 laser as a source, and SF_6 as a photosensitizer, the absorption spectrum of SF_6 in the neighbourhood of its υ_3 (triply degenerate S–F stretching) vibration at 948 cm^{-1} has been the subject of intense scrutiny in the past few years.[55] The rotation–vibration structure is very dense and complex. Its experimental resolution requires sophisticated laser spectroscopic techniques, and its interpretation presents a considerable theoretical challenge; only recently has significant progress been made.[56] Of course, for the process of multiple photon absorption, which almost certainly occurs to some extent in IR LPHP, excited state spectroscopy is also necessary. This work is also stimulated by the use of SF_6 as a target molecule for $^{32}S:^{34}S$ isotope separation.[57] Perhaps of more immediate significance here are the measurements of Nowak and Lyman,[44] who reported absorptions by SF_6 of a number of commonly used CO_2 laser lines over temperatures ranging from 300 to 1800K. The absorption is highly temperature dependent: for the 10P(20) line at 944 cm^{-1}, for example, it falls from 1.0×10^7 mol^{-1} cm^2 at 300K to 1.3×10^5 mol^{-1} cm^2 at 1700K. These measurements have a considerable bearing on estimates of power absorption in the IR LPHP arrangement, of course. In some early estimates of temperatures produced in the pyrolysis cell, this temperature variation was neglected, and this led to very considerable errors.[10] The same is true for some early experiments involving the interpretation of changes in reaction rates as the exciting laser frequency is varied.[58]

B. Photosensitizer Photophysics.—The next step to be considered is the fate of the absorbed IR energy. Work on energy disposal in the laser irradiated SF_6 has, if anything, been even more abundant than that on its absorption spectrum. This work has considered both singly excited (*i.e.*, $\upsilon_3 = 1$) SF_6, and the more challenging problem of multiple photon excitation.[59] The details of such processes are of fundamental significance in IR LMPD, of course, but as far as simple continuous or pulsed IR LPHP is concerned, the central feature of interest is the rate at which the absorbed IR energy appears as translational energy in the reaction mixture. This is of particular importance in pulsed applications, where pyrolysis effectively takes place within a time scale of a few μs.[23]

A recent study by Sugawara *et al.*[40] has reported the time development of vibrational, rotational, and translational effective temperatures in CO_2-laser pulse irradiated SF_6. Since direct measurement using the IR spectrum of SF_6 is precluded by its dense structure, measurements were carried out using tunable

---

[55] C. Bordé and C. J. Bordé, *Chem. Phys.*, 1982, **71**, 417; 1984, **84**, 159.

[56] B. Bobin, C. J. Bordé, J. Bordé, and C. Bréant, *J. Mol. Spectrosc.*, 1987, **121**, 91.

[57] V. Yu. Baranov, E. P. Velikhov, S. A. Kazakov, Yu. R. Kolomiiskii, V. S. Letokhov, V. D. Pis'mennyi, E. A. Ryabov, A. I. Starodubtsev, *Sov. J. Quantum Electron (English translation)*, 1979, **9**, 486.

[58] R. N. Zitter and D. F. Koster, *J. Am. Chem. Soc.*, 1976, **98**, 1613; *ibid.*, 1977, **99**, 5491.

[59] *e.g.*, M. Lenzi, E. Molinari, G. Piciacchia, V. Sessa, and M. L. Terranova, *Spectrochim. Acta, Part A*, 1987, **43**, 137; *Chem. Phys.*, 1990, **142**, 463 and 473; D. W. Lupo and M. Quack, *Chem. Rev.*, 1987, **87**, 181; J. I. Steinfeld, *Spectrochim. Acta, Part A*, 1987, **43**, 129; and references therein.

diode IR laser spectroscopy of an added trace of CO, which has a much simpler vibration–rotation spectrum. Estimates of the vibrational temperature were deduced from measurements of the intensity of the $v = 2 \longleftarrow 1$ hot band; those of the rotational temperature were obtained from the intensity distribution within rotational components of the $v = 1 \longleftarrow 0$ fundamental band; and the translational temperature was measured using the Doppler width of these components. Sugawara *et al.* found that, at total pressures of 1 torr, the rise time of the rotational and translational temperature was 30 μs, whereas that of the vibrational temperature was about 1 ms. These workers were also able to measure the rate of establishment of temperature equilibrium in the cell contents by monitoring the concentration of CO in the same way. From these results, it can be concluded that under normal working conditions the IR radiation appears as heat in times much less than 1 μs, and that a thermal steady state is established over a period of a few ms. Self-consistency in these measurements was established by a close agreement for temperature rises observed and calculated using a simple equipartition of the absorbed energy.

Similar investigations have been carried out by Smith and Laine[60] and McMillen *et al.*[23] as part of their validation experiments using pulsed IR LPHP. These workers monitored the rise of IR fluorescence from a trace of CO or CH_4 added to the IR LPHP gas mixture (SF_6 with either SO_2 or CO_2 added as a bath gas) following exposure to short (μs) CO_2 laser pulses. They showed that the onset of fluorescence follows on very rapidly (much less than the time resolution of the equipment used) after the laser pulse, followed by a drop in a time period of a few μs as the heated wave expands outwards. Similar conclusions have been drawn from studies by Dai *et al.*[61] and Tsang and co-workers.[51,62]

C. Temperature Profiles in the Laser-heated Gas.—As already indicated, the central feature of the IR LPHP technique is the generation of a non-uniform temperature profile within the pyrolysis cell. This is the source of the major advantages of the technique, since it permits the study of reactions under unambiguously wall-less conditions, and the isolation of otherwise unobservable intermediates.[63] Perversely, it is also the root of the major problem in quantitative kinetic studies, since reaction proceeds at very different rates at locations throughout the cell. For this reason, considerable efforts have gone into both the theoretical characterization and experimental measurement of the temperature profiles generated within the cell.

The calculation of the temperature distribution is a complex problem, involving a large number of factors. A complete calculation must include the

---

[60] G P Smith and R M Laine, *J Phys Chem*, 1981, **85**, 1620

[61] H-L Dai, E Specht, M R Berman, and C B Moore, *J Chem Phys*, 1982, **77**, 4494, also M R Berman, P B Comita, C B Moore, and R G Bergman, *J Am Chem Soc*, 1980, **102**, 5694

[62] W Braun and W Tsang, *Chem Phys Lett*, 1976, **44**, 354, D Gutman, W Braun, and W Tsang, *J Chem Phys*, 1977, **67**, 4291

[63] A S Grady, A L Mapplebeck, D K Russell, and M G Taylorson, *J Chem Soc*, *Chem Commun*, 1990, 929

extent of absorption of laser radiation by the photosensitizer, which is, of course, power, temperature, and density dependent.[44] Furthermore, heat transport within the cell by the processes of both conduction and convection is also temperature and pressure dependent. The detailed profile and wavelength of the laser beam, and the effect of heat released in any chemical reaction must also be considered. Neither is the verification of calculation straightforward. Precisely located, but invasive, techniques such as the introduction of microthermocouples can produce quite significant perturbations, particularly if they are placed directly in the path of the laser beam. On the other hand, any external method such as the use of standard reactions of well-known kinetic parameters (the 'chemical thermometer',[10]) can measure only spatially-averaged temperatures, and are therefore of only limited value. In describing some of the efforts to surmount these problems reported in the literature, I shall chart the approximately chronological development in the sophistication of both calculation and measurement.

Once again, we may take as a starting point the work of Shaub and Bauer.[10] These workers attempted to calculate the temperature distribution within the cell, allowing for thermal conduction as the only mode of heat transport. They calculated temperatures which were clearly at odds with those deduced from observed chemical conversion rates, being far too high. Although they attributed these errors to the neglect of convection, it is more likely that the neglect of temperature dependence of both the absorption of the IR radiation by the photosensitizer and thermal conductivity was the major problem. In an effort to demonstrate the significance of convection, they carried out experiments on the rate of the well-known unimolecular conversion of cyclopropane into propene in a three-compartment cell irradiated both vertically (from below or above) and horizontally. Considerable differences in the extent of conversion in the three compartments were found, which were considered to indicate the importance of convection; however, the experimental conditions employed (short irradiation times and narrow cells) were precisely those which emphasize the effects of convection, and the applicability of these results under more commonly employed conditions is not clear.

Shaub and Bauer also pioneered the 'chemical thermometer' technique in this work. In this method, the reaction under study is compared with one of known kinetic characteristics, either in the same pyrolysis cell, or in an identical second cell. Shaub and Bauer compared a number of well-characterized unimolecular reactions in this way, and obtained self-consistent results (to within a few percent). While this method can be useful (and indeed has been widely used), it does have a number of drawbacks. The first of these is the difficulty in matching cells precisely—a very slight mismatch in, for example, window transmission or photosensitizer partial pressure can easily modify the effective pyrolysis temperature by 10 or 20 K. Ideally, one would place both the unknown and standard reactions in the same cell, but this is only possible in the case of non-interfering reactions of the type studied by Shaub and Bauer.[10] Of more serious consequence is the requirement that the unknown and standard reactions have very similar kinetic characteristics. Such a standard can, of course, be found in some cases, but for more complex radical or unknown mechanisms it may simply not be possible to find a sufficiently closely matching reaction.

Zitter *et al.*[32,64,65] refined the calculations of Shaub and Bauer by accounting for the temperature dependence of conductivity k in an empirical form

$$k_T = k_{300}(T/300)^m \qquad (1)$$

which fits fairly well to known data, and leads to a soluble form for the heat conduction equation. The exponent m was taken as a variable parameter. They solved the equation of conduction in the pyrolysis cell, taking into account radial (but not axial) heat conduction, and neglecting convection. This latter they justified on the basis of observing no difference in conversion rates in horizontally or vertically irradiated cells. Apart from the neglect of axial heat flow (which is not justified), they apparently neglected the very strong temperature dependence of absorption. These workers compared the results of their calculations with measurements by interferometry. In this, the local density decrease associated with the local rise in temperature of the laser-heated gas is measured using the change in refractive index; the latter is conveniently measured by counting the number of intensity cycles (fringes) produced in an interferometer with a helium-neon laser as a source. This method can only measure a temperature average along the sight of path of the He–Ne laser beam, which was chosen to coincide with that of the CO_2 laser in the experiments of Zitter *et al.* They found fairly good agreement (1%) between observed and calculated temperatures; an incidental, but significant, result from their work was the confirmation that the steady state temperature profile in the cell was established within about 50 ms of initiation of radiation.

In 1984, Kubat and Pola reported measurements using microthermocouples introduced directly into the cell,[25] an idea presented earlier by Schuster and Li in theses and conference proceedings.[66] Their measurements suggested that convection within the cell was important. This conclusion they based on the observation that while a cylindrically symmetrical temperature distribution was observed when the cell was irradiated vertically, in a horizontally heated cell the temperature maximum lay above the incoming laser beam centre. However, in their work no mention is made of correcting for the perturbing influence of the thermocouples, the most important of which is conduction of heat through the leads; thus the significance of these results is not clear. They supported their measurements by calculations based on the same assumptions as Zitter *et al.*[32,64,65]

Perhaps the most reliable calculations performed to date, neglecting convection,

---

[64] R N Zitter, D F Koster, A Cantoni, and A Ringwelski, *High Temp Sci*, 1980, **12**, 209

[65] R N Zitter, D F Koster, A Cantoni, and A Ringwelski, *Chem Phys*, 1981, **57**, 11

[66] J P Schuster, M Sc Thesis, Cornell University, Ithaca, NY, 1979, W O Li, M Sc Thesis, Cornell University, Ithaca, NY, 1980, J P Schuster, W O Li, and W J McLean, 15th AIAA Thermolysis Conference, Snowmass, CO, 1980

are those of Zhu and Yeung.[67] These workers solved the conduction equation within the cell taking into account both the spatial intensity distribution of the laser beam, and the temperature variation of density, conductivity, and IR absorption of the cell contents. The conduction equation was solved numerically by dividing the cell into thin slices along its axial length, and iterating the radial heat flow within each slice; the absorption was then calculated to provide the power incident on the next slice. This necessitated the artificial device of 'buffer zones' at the front and rear windows, and for this reason their axial temperature distributions are probably unreliable. However, the maximum temperatures calculated agree reasonably well with those deduced from kinetic studies, and by adjusting the thickness of the buffer zones, they were able to match calculated and observed transmissions of laser radiation through the cell.

The most detailed and sophisticated calculations and measurements are those of Horn *et al.*[26] These workers included temperature variations of thermal and absorption parameters, and also included convection in their calculations. They also measured temperature distributions using thermocouples, but they did consider the corrections to be made for the effects of conduction and radiation losses introduced thereby. Their calculated and measured temperature profiles were in very good agreement. As an example of their calculations and measurements, in a vertically oriented cell of length 9.6 cm and internal diameter 3.5 cm, filled with SF_6 (2.25 torr) and Ar (50 torr) and irradiated with 10 W IR laser power in a Gaussian beam of radius 0.7 cm, they calculated maximum temperatures of 900—1000 K. They also found a maximum convective gas velocity of about 20 cm s^{-1}.

In our own laboratory, we have made measurements of the temperature distribution by adding a small partial pressure (<0.5 torr) of unreactive CO to the reaction mixture, and observing the intensities of vibration–rotation components using tunable diode laser spectroscopy.[68] In order to get a complete as possible picture of the distribution, we have used a cell fitted with an additional pair of CaF_2 windows running the length of the cell walls for perpendicular viewing (see Figure 3).

Non-uniformity of the temperature along the path of the probing diode laser beam (of diameter <1 mm) is indicated by a deviation from the Boltzmann distribution in the vibration–rotation component intensities. Although a complete picture of the distribution has yet to be obtained, two conclusions can already be drawn:

(i) the maximum of the temperature distribution is not at the front window, but some 3 cm along the axis, even with horizontal irradiation. This emphasizes the importance of including axial heat conduction in the calculation of profiles.

(ii) we find no significant deviation from cylindrical symmetry in the

---

[67] J. Zhu and E. S. Yeung, *J. Phys. Chem.*, 1988, **92**, 2184.

[68] G. A. Atiya, D. A. Pape, and D. K. Russell, unpublished results; G. A. Atiya, Ph.D. Thesis, University of Leicester, 1990.

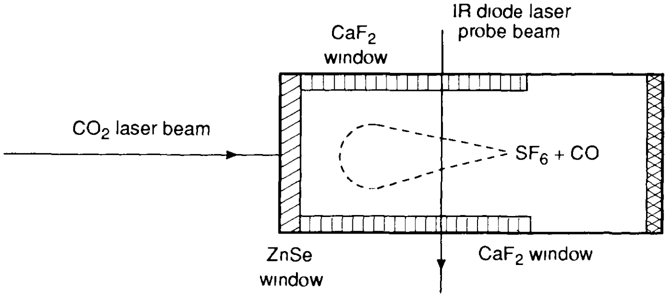

Figure 3 *Arrangement for the measurement of temperature profiles in IR LPHP using TDL spectroscopy The dotted line represents a schematic isotherm in the laser-heated gas mixture, compare Figure 5*

temperature distribution, even with horizontal irradiation. This suggests that convection is of little importance in our particular configuration.

Otherwise, we find results similar to those of other workers. A plot of mean temperature along the probe beam path through the axis of the cell *versus* laser power for two positions along the cell is presented in Figure 4. In the same diagram we present a plot of the mean temperature in the cell derived from measurements using ethyl ethanoate as a chemical thermometer.[10] The difference between the two sets of results emphasizes the necessity for finding a reaction closely matching the unknown in activation energy. In the results presented in Figure 4, the spectroscopic measurements effectively measure the mean temperature using a low energy (10—20 kJ mol^{-1}) probe, whereas the pyrolysis measurements use a high energy (200 kJ mol^{-1}) probe, and the difference in the two measurements is very significant.

We have also investigated means of visualizing the temperature distribution by inducing chemiluminescent reactions in the cell.[69] Figure 5 shows a photograph of the luminescence produced on irradiating a mixture of I_2 vapour and SF_6 with 30 W of CO_2 laser power: this power is very much higher than that normally used in our experiments, since it is sufficient to initiate pyrolysis of the SF_6 itself. We have not investigated the origin of the luminescence, but it probably arises from reaction of F atoms with I_2, or perhaps simply from excited I_2^* produced by recombining I atoms. In any event, it is very apparent from Figure 5 that the temperature maximum is some 2 cm from the entrance window, and that the temperature distribution is indeed cylindrically symmetrical (the photograph represents a sideways view during horizontal irradiation).

It will be apparent from the above discussion that the question of the importance of convection as a mode of heat transport is a contentious and unsettled one, with investigators coming down more or less equally on opposite sides. It is likely that the importance varies with the precise conditions. As pointed out by Zitter *et al.*,[32] it is less likely to be of importance in situations

[69] G A Atiya, A S Grady, and D K Russell, unpublished results, G A Atiya, Ph D Thesis, University of Leicester, 1990

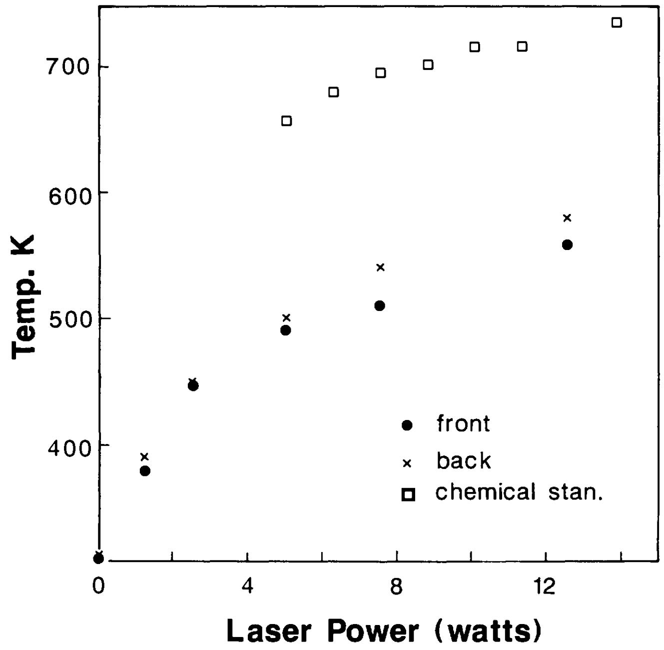

Figure 4 *Mean temperatures in IR LPHP measured by TDL spectroscopy at the cell entrance window* (●) *and* 3.8 cm *from the window* (×). *For comparison, temperatures estimated using* $CH_3COOC_2H_5$ *as a chemical thermometer are also presented* (□)

where the heat source in the cell is very narrow compared with the cell diameter, and where steep temperature gradients are generated. This is the situation in our own experiments, where no buffer gas is added to the SF_6-reagent mixture. On the other hand, Krasa *et al.* have found asymmetric temperature distributions (using IR thermovision monitoring) under very similar conditions,[27] so that the question remains open. It may also be that the lower absorption of the laser radiation by the ZnSe window material in our cell reduces surface heating effects in comparison with NaCl. In any event, almost all measurements have indicated that the temperature and any velocity distribution usually become steady in a time ($\ll 1$ s) short compared with reaction times, although some workers have observed long scale oscillations in temperature.[70] For this reason, the question is of less practical consequence than might appear at first sight, as discussed below.

The problems attendant on measurements of temperature distributions in pulsed systems are rather different. It might appear that one has simply compounded the difficulties described above by adding the extra dimension of temporal variation. However, if experimental conditions are chosen correctly, the

---

[70] K. Ernst and J. J. Hoffmann, *Phys Lett. A*, 1981, **87**, 133; R. T. Bailey, *J. Chem. Phys.*, 1982, **77**, 3453; S. Ruschin and S. H. Bauer, *J. Phys. Chem.*, 1984, **88**, 5042.

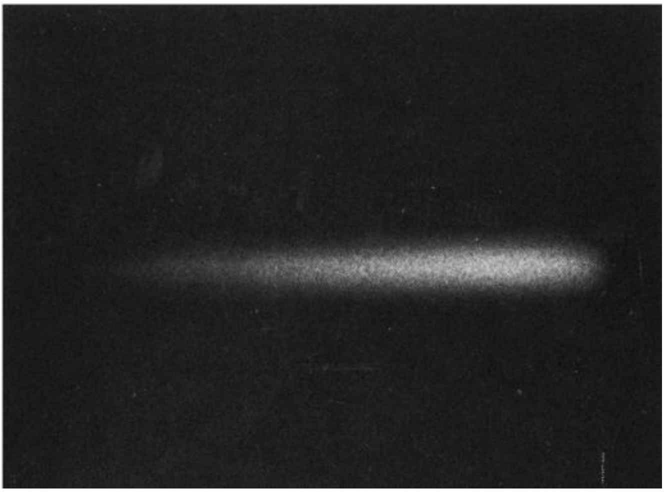

Figure 5 *Photograph of chemiluminescence during IR LPHP of* SF_6 *and* I_2. *The pyrolysis cell is not visible in this photograph; the front cell window is approximately* 1 cm *to the right of the onset of the luminescence, which extends almost to the back window of the* 10 cm *long cell and occupies the axial region of the cell*

use of pulsed sources can actually bring about considerable simplifications in the interpretation of data. This is discussed in detail in two papers by the SRI group.[23,60] The essential feature of the method is that a short pulse (< 1 μs) produces rapid heating within a well-defined volume of the reaction cell, wherein reaction takes place for 5—10 μs until the gas is cooled by expansion. It is apparent from the validation experiments carried out by McMillen *et al.*[23] that the experimental configuration may be designed so that the temperature rise produced in the reaction volume is quite homogeneous, and that reaction may be effectively spatially and temporally defined. This still leaves the problem of actually measuring the temperature produced; this has been achieved by monitoring the IR fluorescence of a small amount of CO or CH_4 added to the system,[23,60] or by studying the Boltzmann distribution in the laser-induced fluorescence of OH radicals.[11] The temperatures measured in this way (1000—1600 K) agree very well with those predicted using a simple calorimetric approach from the energy absorbed. In other pulsed studies of energy transfer, techniques such as diode laser spectroscopy have also been used.[40] These studies have all confirmed the rapid conversion of the IR radiation absorbed into translational energy under normal IR LPHP conditions.

D. Measurement of Kinetic and Thermodynamic Parameters.—Apart from its use in mechanistic studies, the principal application of the IR LPHP technique is in the measurement of reaction rates under rather clearly defined conditions. Because of the homogeneous nature of the heating process, reactions are truly 'wall-less', *i.e.*, they cannot be initiated by surface processes. Moreover, much higher temperatures than in conventional pyrolysis may be routinely used, and attainment of these high temperatures is very rapid, with very little 'dead' or lead-in time. Finally, the rapid diffusion of the products of the primary steps of the reaction sequence out of the hot zone into cool regions of the cell can lead to a simplification of the overall process; it can also lead to the synthesis of otherwise labile products.[63] However, as we have already stated a number of times, the determination of activation energies and other kinetic parameters is far from straightforward. Since this problem is approached rather differently in the case of continuous and pulsed excitation, we shall consider these separately below.

(i) *Continuous Excitation.* If we consider a reaction with a typical activation enthalpy of 250 kJ mol^{-1}, in an IR LPHP cell with a temperature of 1000 K at the maximum and the walls at 300 K the rate of the reaction will vary by a factor of 10^{30} over the cell. Thus as the reaction progresses, reactant and products will rapidly acquire very different concentrations (or, more accurately, partial pressures) throughout the cell. These partial pressure gradients will be attenuated by the processes of diffusion and convection, but it is clear that the overall time and space dependence of partial pressure will be very complex. These factors have led a number of workers to conclude that direct measurement of reaction rates in the continuous IR LPHP process is of little use, and this has led to the development of comparative methods. However, as we have seen above, even this method requires some theoretical justification, and is not without its drawbacks.

Recently, we have shown that, under correctly chosen conditions, the measurement of spatially averaged concentrations (which is automatically realized by monitoring the cell contents in the absence of the laser radiation) can lead to useful kinetic data, provided details of the temperature distribution are known.[71] Details of this will be given elsewhere,[71] but the conclusions are as follows. For a first order reaction, the rate of change of the average concentration c_{av} is given by a first order relation

$$\mathrm{d}c_{av}/\mathrm{d}t = k_{av}\, c_{av} \tag{2}$$

where k_{av} is the spatial average of the position-dependent rate constant $k(r)$ over the cell. This equation holds true provided the diffusion coefficient D and the average rate constant k_{av} obey the relation

$$\pi^2 D/l^2 > k_{av} \tag{3}$$

for the axial length l (or for a box-shaped cell), or

$$3.832^2 D/a^2 > k_{av} \tag{4}$$

for the radius a of a cylindrical cell. These conditions generally hold true for the

---

[71] D. K. Russell, unpublished work; G. A. Atiya, Ph.D. Thesis, University of Leicester, 1990.

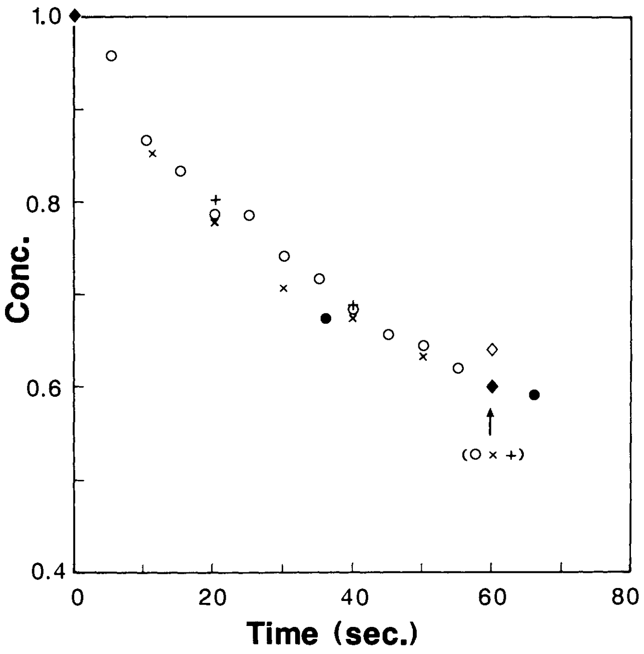

Figure 6 *Normalized FTIR signal of* CH_3CHO *subjected to IR LPHP for a total of* 60 *seconds and a number of exposure times* ◆ = 60 s, ○ = 30 s, + = 20 s, × = 10 s, ○ = 5 s

typical IR LPHP cell, and for reactions whose half life is longer than a few seconds Similar conditions hold for non-first-order reactions[71] This condition represents the most stringent case, totally neglecting the effects of convection (which will undoubtedly relax this requirement) Our conclusion is that measurement of c_{av} can therefore yield useful kinetic data, even if the instantaneous concentration in the cell shows very large variations This conclusion is easily subjected to experimental verification, as shown in Figure 6 This Figure shows the time development of the concentration of ethanal (which, incidentally, is known to undergo pyrolysis according to 3/2 order kinetics) subjected to IR LPHP for a total of 60 seconds, but with irradiation intervals of 5, 10, 15, 20, 30, or 60 seconds The absence of any significant deviations confirms the validity of equation 2 above Similar observations have been made by other workers (*e g*, ref 72), but the effect has been hitherto attributed to the effects of rapid convection, our analysis has shown that it is not necessary to invoke convection as the major mode of redistribution

Having demonstrated the validity of timed measurements of cell-averaged concentrations in the determination of reaction rates, one might enquire if there

---

[72] J Pola *Int J Chem Kinet* 1983 **15** 1119

are methods by which this quantity might be measured *in situ* as the pyrolysis actually proceeds. This would be of considerable benefit, since even the relatively rapid FTIR method is quite time-consuming. What is required is a non-invasive and rapid method of monitoring the entire cell contents—methods such as spectroscopy are not usually applicable, since they generally monitor only a portion of the cell. We have investigated the possibility of using an acoustic resonance frequency of the cell and its contents during irradiation and reaction.[43] A suitable resonance frequency is easily measured by modulating the output power of the laser (by applying an AC voltage to a piezo-electric stack onto which one of laser cavity mirrors is mounted) and observing the resulting photoacoustic wave generated in the cell by means of a small microphone mounted in the wall. Very small ($<1\%$) modulation depths are required, and if a high freqency (a few kHz) resonant mode is chosen, the modulation has little effect on the temperature of the cell. The resonance frequency of the cell is a complex function of the temperature distribution, and also of the mean relative molecular mass of its contents. Thus changes in molecularity are very easily monitored. In Figure 7 we show the results of measurements of the pyrolysis of ethyl ethanoate monitored using both FTIR spectroscopy in the usual way, and the new photoacoustic method. The very close agreement between the two methods is very encouraging, and it seems that the photoacoustic technique may indeed provide accurate rate measurements.

(ii) *Pulsed Excitation.* The difficulties in straightforward measurement of rate parameters described above for continuous excitation have led some workers to investigate the possibilities of pulsed excitation.[54,61,62] The principle of this variation is that a short IR laser pulse produces a very rapid rise in temperature within a precisely defined spatial region of the pyrolysis cell. Pyrolysis then occurs within this region; this proceeds until the heated gas is cooled by expansion into the remainder of the cell. Temperature rises within the 'active' zone can in principle be calculated by simple calorimetry, if the absorbed energy is measured. Clearly, a number of approximations have been made in this simple analysis. The principal of these are that the reaction zone is precisely limited, that the reaction temperature is uniform within this zone, and that a reaction time can be defined.

The credit for the invention of this method probably lies with Tsang and co-workers,[62] and other early investigations were carried out by the groups of Moore[61] and Steel.[54] The most detailed description of the method, including a very careful consideration of the approximations involved and a considerable number of investigative experiments, has been provided by McMillen *et al.*,[23] and this work is highly recommended as a particularly readable account of this application of the techinique. In addition to verifying the validity of the approximations described above for unimolecular reactions, these workers have shown that the technique can provide unequivocal information about radical reactions, such as the pyrolysis of azo compounds. A number of other results are discussed in the case studies below.

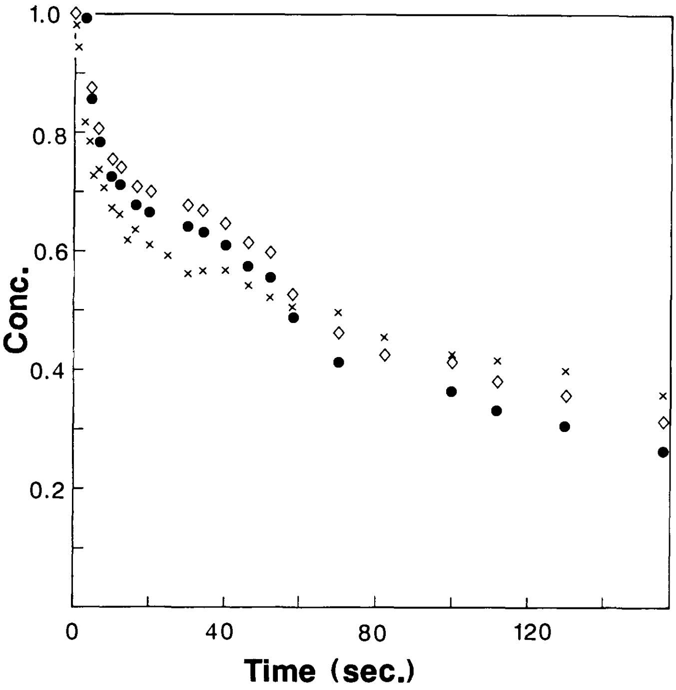

Figure 7 *Progress of the IR LPHP of* $CH_3COOC_2H_5$ *monitored using FTIR spectroscopy (×) and the acoustic cell resonance frequency (● and ◇) The two sets of resonance frequency results arise from the use of different approximations in the calculations*

5 Three Case Studies

In this final section, I shall describe three areas of research in which the IR LPHP technique has been utilized to good effect Inevitably, this represents something of a personal selection, and there is of course some degree of overlap among these three topics Nonetheless, the examples chosen are representative of investigations currently exploiting the unique characteristics of the method

A. Studies of Halogenated Organic Pyrolysis Mechanisms.—The pyrolysis of organic molecules, especially those containing halogens, has been a happy hunting ground for the IR LPHP experimenter A selection of these is presented in Table 1, by and large, studies of IR LMPD have been omitted, since the motivation of this type of work is usually somewhat different

A considerable number of the reactions listed in Table 1 are effectively dehydrohalogenations An excellent summary of some of this work has been presented by Pola,[12] and the examples used in this section draw heavily on this author's work In many cases, the principal differences between mechanisms in conventional (hot-wall) pyrolysis and in IR LPHP may be ascribed to the complete suppression of wall-initiated reactions, in particular radical chain processes. A good example is that of allyl chloride.[73] In conventional pyrolysis, a wide range of polymeric products is observed,[74] whereas under IR LPHP only propyne, propadiene, benzene, and HCl are formed in significant quantities. These observations are readily rationalized in the scheme below:

$$\mathrm{CH_2{=}CH{-}CH_2Cl} \xrightarrow[-\mathrm{Cl}]{} \mathrm{CH_2{=}CH{-}CH_2} \xrightarrow[-\mathrm{HCl}]{\mathrm{Cl}} \mathrm{CH_2{=}C{=}CH_2} \longrightarrow \mathrm{CH_3{-}C{\equiv}CH} \qquad (5)$$

$$\mathrm{CH_2{=}CH{-}CH_2Cl} \xrightarrow[-\mathrm{HCl}]{\mathrm{Cl}} \mathrm{CH_2{=}CH{-}CHCl} \longrightarrow \tfrac{1}{2}\mathrm{C_6H_6} + \mathrm{HCl} \qquad (6)$$

On the hot walls of conventional pyrolysers, these steps are followed by further reaction of the propyne and propadiene.

A second illustration comes from the investigation of polychlorinated ethanes by Pola and co-workers[46,61,73] and by Holbrook *et al.*[34] In these systems, the IR LPHP process at low laser power (*i.e.*, temperature) results in a purely molecular elimination of HCl, as shown by the lack of any effect on addition of well-known Cl and alkyl radical traps. On the other hand, in hot-wall pyrolysis (and also IR LPHP at higher laser power[34]), more complex radical chain reactions lead to a much wider range of observed products, and a sensitivity to radical traps.

Two other investigations are worthy of particular note. The first is a comparative study of the IR LPHP of CH_3CCl_3, CH_3SiCl_3, and CH_3GeCl_3.[46] The first of these is pyrolysed *via* a molecular elimination, as described above. This pathway is not favoured for the latter two, since Si=C and Ge=C bonds are not stable. In these cases, the reaction therefore proceeds *via* a radical mechanism. Interestingly, the case of CH_3SiCl_3 provides one of the few instances where the SF_6 plays a part in the reaction; the abstraction of F from SF_6 by Si-centred radicals is amply attested in other studies.[75] Finally, IR LPHP has proved its worth in industrial applications. Commercially available germanium tetrachloride contains up to 1000 ppm of organic chlorides and bromides, but its use as a precursor for Ge-doping in fibre optics requires a level of these contaminants below 50 ppm. Pola demonstrated that these impurities are readily and selectively removed by using IR LPHP.[76] The method has also been used in the purification of other precursors for the semi-conductor and other industries, notably $AsCl_3$,[77] SiH_4,[78] and BCl_3.[79]

B. Organometallic Pyrolysis Mechanisms.—A second area where the IR LPHP has proved of particular value is in the study of the pyrolysis mechanisms of

[73] J. Pola, *J. Chem. Soc., Perkin Trans. 2*, 1983, 231.

[74] S. Kunichika, Y. Sakakibara, and M. Taniuchi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1082.

[75] I. M. T. Davidson and C. E. Dean, *Organometallics*, 1987, **6**, 966.

[76] J. Pola, M. Farkacova, and V. Chvalovsky, *J. An. App. Pyr.*, 1985, **7**, 351.

[77] R. V. Ambartzumian, Yu. A. Gorokhov, S. L. Grigorovich, V. S. Letokhov, G. G. Makarov, Yu. A. Malinin, A. A. Puretskii, E. P. Filippov, and N. P. Furzikov, *Kvanovaya Elektron. (Moscow)*, 1977, **4**, 171.

[78] S. M. Freund and W. C. Danen, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 45.

[79] J. A. Merritt and L. C. Robertson, *J. Chem. Phys.*, 1977, **67**, 3545.

Table 1 *Representative halogenated organic compounds studied by IR LPHP*

Compound	*Photosensitizer*	*Reaction products and comments*	*Ref*
CF_2Cl_2	None or SF_6	$C_2F_4Cl_2 + Cl_2$, variation with laser wavelength observed	*a*
$C_2H_2F_2$	SF_6	*cis* $\longrightarrow$ *trans*, and *trans* $\longrightarrow$ *cis*	*b*
$C_2H_2Cl_2$	SF_6	*cis* $\longrightarrow$ *trans*, and *trans* $\longrightarrow$ *cis*	*b*
$CH_3CHClCH_3$	SF_6	Dehydrochlorination	*b*
CF_2Cl_2	SF_6	Various products	*b*
CHF_3	SF_6	Various products	*b*
$CHClF_2$	SF_6	Various products	*b*
cyclo-C_4F_8	SF_6	C_2F_4, C_3F_6	*b*
$(CH_3)_3CCl$	SF_6	Dehydrochlorination	*b*
$CHClF_2 + N_2O$	SF_6	CF_2O, HCl	*b*
$CHBr_3$	SF_6	Brominated alkenes	*b*
CH_2Br_2	SF_6	Brominated alkenes	*b*
C_2F_6	SF_6	C_2F_4	*b*
CF_2ClCF_2Cl	None or SF_6	Various, mainly C_2F_4 and CF_2Cl_2	*c*
CF_2ClCF_2Cl	None or SF_6	Various, as above	*d*
CH_3CF_2Cl	None	Dehydrochlorination to CH_2CF_2, enthalpy limit deduced	*e*
CH_3CF_2Cl	None	Activation enthalpy, $CH_3COOC_2H_5$ used as 'chemical thermometer'	*f*
CH_3CF_2Cl	None	Reaction kinetics investigated	*g*
cis-3,4-dichlorocyclobutene	None	Dichlorobutadienes, Woodward–Hoffmann rules obeyed	*h*
CH_3I, CD_3I	SF_6	CH_4, C_2H_6, C_2H_4, C_2H_2, I_2, isotope effects, wavelength dependent	*i*
CF_3COOH	SF_6	CF_2O, CO, CF_3CFO (and minor products)	*j*
$(CF_3CO)_2O$	SF_6	CF_2O, CO, CF_3CFO (and minor products)	*k*
CH_3CCl_3	SF_6	Dehydrochlorination to $CH_2{=}CCl_2$	*l*
CH_3SiCl_3	SF_6	Reaction of silyl radicals with SF_6, SiF_4 observed	*l*
CH_3GeCl_3	SF_6	HCl, CH_4, $GeCl_3H$, no reaction with SF_6 observed	*l*
$(COCl)_2$	SF_6	$COCl_2$, CO $(+Cl_2)$, no radicals trapped	*m*
$CH_3CH_2CHBrCH_3$	SF_6	Pulsed, dehydrobromination, used as a reference reaction	*n*
$CH_2ClCHClCH_3$	None or SiF_4	Many channels yielding isomeric chloropropenes	*o*

Table 1—*continued*

Compound	*Photosensitizer*	*Reaction products and comments*	*Ref.*
C_2H_5Cl	SiF_4	Dehydrochlorination to C_2H_4; used as a standard	*p*
CH_3CCl_3	SiF_4	Dehydrochlorination to $CH_2{=}CCl_2$	*p*
$CH_2ClCHCl_2$	SiF_4	Dehydrochlorination to *cis* or *trans* CHClCHCl; no CH_2CCl_2	*p*
$CH_2{=}CHCH_2Cl$	SF_6	HCl, CH_3CCH, CH_2CCH_2, C_6H_6; no polymeric products	*q*
CH_3CCl_3	SF_6	Molecular dehydrochlorination; conventional pyrolysis radical chain	*r*
CH_3CCl_3	SF_6	Dehydrochlorination; kinetic studies	*s*
C_2H_5Br	SF_6	Molecular dehydrobromination; conventional pyrolysis radical chain	*t*
C_3H_7Br	SF_6	Molecular dehydrobromination	*t*
Various chloroethanes	SF_6	Mechanistic study of dehydrochlorination reactions	*u*
RCl and RBr	SF_6	Used to remove halocarbon impurities from $GeCl_4$	*v*
C_2F_4	SF_6	Reaction with O_2; dioxetane intermediates proposed	*w*, *x*, *y*
C_5F_{10}	SF_6	Reaction with O_2; dioxetane as intermediate	*y*
Various chlorocarbons	SF_6	Mechanistic investigation using radical traps	*z*
$CF_3OCF_2CF_2I$	SF_6	Radical reaction mechanism	*aa*
$CHBrClCF_3$	SF_6	Many products	*bb*
$CF_3CFCFCF_3$	SF_6	Reaction with O_2 proceeds *via* a dioxetane	*cc*
$(R_fCO)_2O$	SF_6	$R_f = CF_3, C_2F_5, C_3F_7$	*dd*

[a] R. N. Zitter, R. A. Lau, and K. S. Wills, *J. Am. Chem. Soc.*, 1975, **97**, 2578. [b] Ref. 10. [c] Ref. 58. [d] Ref. 58. [e] R. N. Zitter and D. F. Koster, *J. Am. Chem. Soc.*, 1978, **100**, 2265. [f] Ref. 31. [g] Ref. 65. [h] W. C. Danen, D. F. Koster, and R. N. Zitter, *J. Am. Chem. Soc.*, 1979, **101**, 4281. [i] Ref. 35; G. A. Atiya, R. Maw, D. K. Russell, S. Salfity, and M. Ward, unpublished results. [j] J. Pola, *Collect. Czech Chem. Commun.*, 1981, **46**, 2854. [k] J. Pola, *Collect. Czech. Chem. Commun.*, 1981, **46**, 2860. [l] Ref. 46. [m] J. Pola, *Collect. Czech. Chem. Commun.*, 1982, **47**, 3258. [n] Ref. 23. [o] Ref. 51. [p] Ref. 61. [q] Ref. 73. [r] Ref. 72. [s] P. Kubat and J. Pola, *Collect. Czech. Chem. Commun.*, 1985, **50**, 1537. [t] P. Kubat and J. Pola, *Collect. Czech. Chem. Commun.*, 1985, **50**, 1548. [u] Ref. 34. [v] Ref. 75. [w] J. Pola and J. Ludvik, *Spectrochim. Acta, Part A*, 1987, **43**, 297. [x] J. Pola and J. Ludvik, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1727. [y] P. K. Chowdhury, J. Pola, K. V. S. Rama Rao, and J. P. Mittal, *Chem. Phys. Lett.*, 1987, **142**, 252. [z] P. Kubat and J. Pola, *Z. Phys. Chem. (Leipzig)*, 1987, **268**, 849. [aa] J. Pola, *J. An. App. Pyr.*, 1988, **13**, 151. [bb] J. Pola and Z. Chvatal, *J. Fluorine Chem.*, 1989, **42**, 233. [cc] J. Pola and J. Vitek, *Collect. Czech. Chem. Commun.*, 1989, **54**, 3083. [dd] P. Kubat and J. Pola, *Collect. Czech. Chem. Commun.*, 1990, in press

organometallic compounds. Simple organometallic compounds of modest volatility have leapt to prominence recently as highly practical precursors to the deposition of metals and metal oxides for applications such as semi-conductors, solar cells, and fibre-optics.[80] A typical example is trimethyl gallium in the metal–organic chemical vapour deposition (MOCVD) of gallium arsenide:[81]

$$Ga(CH_3)_3 + AsH_3 \longrightarrow GaAs + 3CH_4 \qquad (7)$$

Clearly, the design of custom-made precursors for new materials requires an understanding of the mechanisms of pyrolysis of such compounds, and here fundamental information is lacking. The reason for this is very simple; many such compounds are notoriously air and moisture sensitive, and attempts to study their pyrolysis have often been frustrated by surface reactions. A typical example comes from the oxidation of tetramethyl tin in the production of SnO_2; the oxide layer thus produced is highly auto-catalytic (as shown by observed zero-order kinetics), and thus it is almost impossible to study the homogeneous pyrolysis by conventional methods.[82] The technique of IR LPHP is ideally suited to this kind of problem, and indeed a number of studies have been conducted. A selection of these is listed in Table 2. I have excluded from consideration compounds of B, Si, and Ge,[83,84] although a considerable quantity of work has been carried out on such systems. I have, however, also included carbonyls, since many of the above remarks also apply to these compounds.

As an example of the utility of the IR LPHP technique in the study of organometallic reaction mechanisms, I shall consider work carried out in our own laboratory over the past two years.[85–91] For the most part, this has been concentrated on the mechanisms of pyrolysis of the simple alkyls of Group III metals and their derivatives. Much of this work has been directed towards an understanding of the characteristics required of suitable precursors for the deposition of Ga (in GaAs) and Al (in AlGaAs).

The most widely used organoaluminium precursor is trimethyl aluminium,

---

[80] P D Dapkus, *Annu Rev Mater Sci*, 1982, **12**, 243

[81] 'Gallium Arsenide and Related Compounds 1980', ed H W Thim, Institute of Physics, London, 1981

[82] A P Ashworth, E N Clark, and P G Harrison, *J Chem Soc*, *Chem Commun*, 1987, 782

[83] *e g*, A M Barriola, C Manzanares, and J de Jesus, *Inorg Chim Acta*, 1985, **98**, L43, A M Barriola and L A Valcarcel, *Spectrochim Acta, Part A*, 1990, **46**, 449

[84] H M Frey, A Kashoulis, L N Ling, I M Pidgeon, and R Walsh. *J Chem Soc*, *Chem Commun*, 1981, 915, J Pola, V Chvalovsky, E A Volnina, and L E Guselnikov, *J Organomet Chem*, 1988, **341**, C13, J Pola, E A Volnina, and L E Guselnikov, *J Organomet Chem*, in press

[85] A S Grady, M P Coogan, M D Robertson, and D K Russell, *J Cryst Growth*, to be submitted

[86] A S Grady, R D Markwell, and D K Russell, *J Chem Soc*, *Chem Commun*, submitted for publication

[87] A S Grady, S G Puntambekar, and D K Russell, *Spectrochim Acta, Part A*, to be published, *J Organomet Chem*, to be submitted

[88] A S Grady, R D Markwell, and D K Russell, unpublished results

[89] A S Grady, R D Markwell, D K Russell, and A C Jones, *J Cryst Growth*, 1990, **106**, 239

[90] A S Grady, R D Markwell, D K Russell, and A C Jones, *J Cryst Growth*, to be published

[91] G A Atiya and D K Russell, unpublished results, G A Atiya, Ph D Thesis, University of Leicester, 1990

Table 2 *Representative organometallic compounds studied by IR LPHP*

Compound	*Photosensitizer*	*Reaction product and comments*	*Ref.*
$Fe(CO)_5$	SF_6	Fe + CO	*a*
$Fe(CO)_5 + O_2$	SF_6	Iron oxides + CO	*a*
$Fe(CO)_5$	SF_6	Pulsed; bond enthalpy determination	*b, c*
$Fe(^{12}CO)_5 + {}^{13}CO$	SF_6	CO exchange	*d*
$Fe(CO)_5 + PF_3$	SF_6	CO–PF_3 exchange	*d*
$Cr(CO)_6$	SF_6	Pulsed; bond enthalpy determination	*c*
$Mo(CO)_6$	SF_6	Pulsed; bond enthalpy determination	*c*
$W(CO)_6$	SF_6	Pulsed; bond enthalpy determination	*c*
$Me_2Os(CO)_4 + CO$	SF_6	$Os(CO)_5$	*d*
$H_2Os(CO)_4 + CO$	SF_6	$Os(CO)_5$	*d*
$Os(^{12}CO)_5 + {}^{13}CO$	SF_6	CO exchange	*d*
$HMn(CO)_5 + CO$	SF_6	H–CO exchange	*d*
MR_n	SF_6	Various metals and metal alloys from alkyls	*e*
$Ge(OCH_3)_4$	None	Isotope separation	*f*
$Zr(OBu^t)_4$	None	Isotope separation	*f*
$U(OCH_3)_6$	None	Isotope separation; molecule 'tailored' to IR LPHP	*g*
$Al(CH_3)_3$	SF_6	$Al(CH_3)_2$ radical trapped with SF_6 or CCl_4	*h*
$Ga(CH_3)_3$	SF_6	CH_3 radical trapped with D_2	*i*
$Ga(C_2H_5)_3$	SF_6	$Ga(C_2H_5)_2H$ and $Ga(C_2H_5)H_2$ isolated	*j, k*
$Al(CH_3)_2H$	SF_6	Alternative Al MOCVD precursor to $Al(CH_3)_3$	*l*
$AlH_3{\cdot}N(CH_3)_3$	SF_6	Alternative clean Al precursor	*m*
$AlH_3{\cdot}N(CH_3)_3$	SF_6	Mixtures with $Ga(CH_3)_3$ and $Ga(C_2H_5)_3$ studied	*n, o*
$Sn(CH_3)_4$	SF_6	Precursor for Sn in MOCVD	*p*
$Sn(CH_3)_4 + O_2$	SF_6	Precursor for SnO_2; auto-catalysed in conventional pyrolysis	*p*
$Ti(OCH(CH_3)_2)_4$	C_2H_4	Precursor for TiO_2	*q*
$(CH_3)Mn(CO)_5$	SF_6	CH_4, CO, and Mn; precursor for Mn MOCVD	*r*
$(CH_3)Mn(CO)_5 + (CH_3)_3SiH$	SF_6	$(CH_3)_3SiMn(CO)_5$; precursor for MnSi deposition	*r*

[a] Ref. 10. [b] Ref. 60. [c] K. E. Lewis, D. M. Golden, and G. P. Smith, *J. Am. Chem. Soc.*, 1984, **106**, 3905. [d] Ref. 24. [e] S. H. Bauer, *Spectrochim. Acta, Part A*, **43**, 227. [f] Y. Okada, S. Kato, S. Satoaka, and K. Takeuchi, *Spectrochim. Acta, Part A*, 1990, **46**, 643. [g] S. S. Miller, D. D. DeFord, T. J. Marks, and E. Weitz, *J. Am. Chem. Soc.*, 1979, **101**, 1036. [h] Ref. 38; G. A. Atiya, A. S. Grady, D. K. Russell, and T. A. Claxton, *Spectrochim. Acta, Part A*, to be published. [i] Ref. 85. [j] Ref. 63. [k] Ref. 87. [m] Ref. 88. [n] Ref. 89. [o] Ref. 90. [p] Ref. 91. [q] G. W. Rice and R. L. Woodin, *Spectrochim. Acta, Part A*, 1987, **43**, 299. [r] A. S. Grady, I. M. T. Davidson, M. Pennington, and D. K. Russell, unpublished results

$(CH_3)_3Al$ However, the pyrolysis of this precursor leads to the incorporation of unwanted carbon in the deposited metal, in direct contrast with the corresponding gallium case[92] Conventional pyrolysis has failed to provide a convincing explanation for this phenomenon,[93] largely because organometallic intermediates produced in the gas phase are very rapidly destroyed on hot walls,[94] and are not therefore detected However, in the IR LPHP of $(CH_3)_3Al$, it is possible to trap the $(CH_3)_2Al^{\bullet}$ radical formed as either the fluoride, $(CH_3)_2AlF$, or chloride, $(CH_3)_2AlCl$[38] Furthermore, we have also shown that it is the monomer (trimethyl aluminium is largely dimeric at room temperature) that undergoes pyrolysis[38] These observations, coupled with the observation of $CH_3^{\bullet}$ radicals in matrix isolation and laser spectroscopic experiments,[95] unambiguously confirm the usual assumption that $Al{-}CH_3$ bond homolysis is the primary step The $CH_3^{\bullet}$ radical can readily abstract H atoms from the parent molecule, leading to the formation of a $>Al{-}CH_2$ bond, *ab initio* calculations[96] have shown this to have considerable double bond character, and therefore increased stability It therefore seems feasible that these processes may be involved in the incorporation of C into deposited Al On the other hand, although the first step in the pyrolysis of $(CH_3)_3Ga$ is also $Ga{-}CH_3$ bond homolysis,[85] the slightly stronger C–H bond in the latter[89] reduces the occurrence of H-abstraction from the parent molecule, and this pathway is no longer significant This has been shown by the IR LPHP of mixtures of $(CH_3)_3Ga$ and D_2 In this system, considerable quantities of CH_3D are produced, whereas in mixtures of $(CH_3)_3Al$ and D_2, no CH_3D is observed[85] Thus in the competition for methyl radicals between D_2 and the parent $(CH_3)_3M$, the D_2 wins when $M = Ga$, but abstraction from the parent is more rapid when $M = Al$ Armed with this insight, we have investigated the pyrolysis mechanisms of some promising alternative Al precursors, such as $(CH_3)_2AlH$[87] and $AlH_3{\cdot}N(CH_3)_3$[88,90]

A second system of considerable interest, both industrially and from a fundamental point of view, is triethyl gallium Compounds of Al and Ga with alkyl groups containing β-hydrogens have long been believed to undergo β-elimination of alkenes on pyrolysis, *e g*

$$(C_2H_5)_3Ga \longrightarrow (C_2H_5)_2GaH + C_2H_4 \qquad (8)$$

However, attempts to isolate the dialkylgallanes thus produced have failed, partly because of the competing reverse reaction, and partly because of subsequent catalysed polymerization of the alkene[97] The IR LPHP technique neatly bypasses these problems, since the relatively involatile diethylgallane

---

[92] T F Kuech, E Veuhoff, T S Kuan, V Deline and R Potenski, *J Cryst Growth*, 1986, **77**, 257

[93] M Suzuki and M Sato, *J Electrochem Soc Solid State Sci Tech*, 1985, **132**, 1684

[94] N Suzuki, C Anayama, K Masu, T Tsubouchi, and N Mikoshiba, *Jap J Appl Phys* 1986 **25**, 1236

[95] J B Raynor personal communication D W Squire, C S Dulcey, and M C Lin, *J Vac Sci Technol*, *B*, 1985, **3**, 1513

[96] T A Claxton, personal communication

[97] J J Eisch, *J Am Chem Soc*, 1962, **84**, 3830

produced is condensed onto the cold walls of the reaction cell, where it can be examined at leisure.[63] Not only that, we have also shown that, under the correct conditions, it is possible to carry out a second β-elimination step, and also isolate the monoethylgallane produced:[86]

$$(C_2H_5)_2GaH \longrightarrow (C_2H_5)GaH_2 + C_2H_4 \qquad (9)$$

This compound has never before been isolated, indeed it is the first demonstrated example of a free monoalkylgallane prepared by any method. As has been hinted by a number of other workers in the field of organometallic pyrolysis,[24] the IR LPHP method opens up reaction pathways not reached by conventional techniques.

C. Quantitative Kinetic Studies.—As a final example of applications of the IR LPHP technique, I shall consider some of the measurements of kinetic parameters (principally activation energies) which have been reported. A selection is given in Table 3; a number of less quantitative results have also been reported. The selection of Table 3 covers most of the variations described in the paragraphs above: continuous wave excitation, using either direct measurement of temperature or the chemical standard technique, and pulsed excitation studies of both unimolecular and bimolecular reactions.

Several aspects of the studies described in Table 3 have already been discussed in the sections above, and I shall restrict my comments at this stage to the results of chemical interest. Of the many applications of the 'chemical thermometer' technique since its invention by Shaub and Bauer,[10] perhaps a typical investigation is that of Lavrushenko *et al.* on the pyrolysis of $SiCl_3H$.[98] In this study, $SiCl_3H$ was pyrolysed in the presence of SiF_4 as a photosensitizer. The reaction produces HCl cleanly, and the $SiCl_2$ simply results in a polymeric deposit on the cold cell walls:

$$SiCl_3H \longrightarrow HCl + SiCl_2 \qquad (10)$$

The reaction was monitored by IR spectroscopy and mass spectrometry of the starting silane and the product HCl. The chemical standard used in this case was 1,1,2,2-tetrafluorocyclobutane, which dissociates through one of two pathways with an activation enthalpy of 292 kJ mol^{-1}.[99] The activation enthalpy determined for the silane decomposition was 295 kJ mol^{-1}.[98] This investigation highlights the simplifying nature of the IR LPHP technique, since the reaction is complicated in conventional pyrolysis by the effects of the silene $SiCl_2$;[100] it also illustrates the necessity to utilise a standard reaction of very similar kinetic characteristics.

---

[98] B. B. Lavrushenko, A. V. Bakianov, and V. P. Strunin, *Spectrochim. Acta, Part A*, 1990, **46**, 479.

[99] R. T. Conlin and H. M. Frey, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 322.

[100] Y. N. Tang, in 'Reactive Intermediates', ed. R. A. Abramovitch, 1982, **2**, Plenum Press, New York, 297.

Table 3 *Representative kinetic studies using IR LPHP*

Compound	*Photosensitizer*	*Mode and comments*	*Ref*
cis ⟶ *trans* 2-butene	SF_6	Continuous wave extensive series of studies demonstrating the 'chemical thermometer' technique for unimolecular reactions with activation energies ranging from 180 to 280 kJ mol^{-1}	*a*
trans ⟶ *cis* 2-butene	SF_6		
cyclopropane ⟶ propene	SF_6		
cis ⟶ *trans* $C_2H_2F_2$	SF_6		
cis ⟶ *trans* $C_2H_2Cl_2$	SF_6		
$CH_3CHClCH_3 \longrightarrow C_3H_6$	SF_6		
cyclo-$C_6H_8 \longrightarrow C_6H_6$	SF_6		
$CCl_3CH_3 \longrightarrow CCl_2CH_2$	SiF_4	Pulsed, temperatures of 1100—1400 K, E_a, A measured C_2H_5Cl used as a standard	*b*
$CHCl_2CH_2Cl \longrightarrow CHClCHCl$	SiF_4		
Cyclobutanone	NH_3	Pulsed, two reaction paths with different E_a	*c*
$CH_3CH_2CHBrCH_3$	SF_6	Pulsed, first three used as test reactions, unimolecular elimination reactions, new results on azo compounds	*d*
$CH_3CO_2CH(CH_3)_2$	SF_6		
$CH_3CO_2C_2H_5$	SF_6		
2,2′-azoisopropane	SF_6	Concerted mechanism suggested	
OH + CH_4	SF_6	Pulsed, first example of bimolecular reaction OH generated from H_2O_2, detected by LIF, temperatures 800—1400 K, difficult to obtain otherwise	*e*
OH + C_3H_8	SF_6		
OH + C_3H_6	SF_6		
$CH_3CF_2Cl \longrightarrow CH_2CF_2$	SF_6	Continuous wave, based on calculated temperatures, E_a found	*f*
$CH_2CO_2C_2H_5 \longrightarrow CH_3CO_2H$	SF_6		
$CH_3CHNO_2CH_3 \longrightarrow$ various	SF_6	Continuous wave, $CH_3CO_2C_2H_5$ as standard	*g*
$SiCl_3H \longrightarrow SiCl_2 + HCl$	SiF_4	Continuous wave, 1,1,2,2-tetrafluorocyclobutane as standard	*h*

[a] Ref 10 [b] Ref 61 [c] Ref 54 [d] Ref 23 [e] Ref 11 [f] Ref 32 [g] J Pola, M Farkacova, P Kubat, and A Trka, *J Chem Soc, Faraday Trans 1*, 1984, **80**, 1499 [h] Ref 98

Of reports using pulsed methods that of Smith *et al.* on the reaction of OH radicals with a number of hydrocarbons is perhaps of special significance as representing the first application of IR LPHP to a bimolecular reaction.[11] In this study, OH radicals were generated by the dissociation of H_2O_2 in the IR laser irradiated region. Here they reacted with the substrate (CH_4 as a diagnostic case, and also propane and propene), the decay in OH concentration being monitored by Laser Induced Fluorescence using a dye laser. At the same time, effective temperatures were determined by monitoring the relative populations of several different rotational levels in the OH radical. Smith *et al.* were able to measure bimolecular rate constants with a typical uncertainty of 15—25% at temperatures up to 1400K, very much higher than in previous studies. These workers have also reported a number of further studies of high temperature reactions of OH radicals, amply demonstrating the usefulness of this particular development.[101]

Acknowledgements. I would like to thank all my co-workers who have collaborated in the studies described above, particularly postgraduate students Ghalib Atiya, David Pape, and Andrew Grady, and post-doctoral research associates Shakher Puntambekar, Ross Markwell, and Mark Pennington. The work has been funded through grants from the DTI and the SERC, and has received active encouragement and support from the MOD and Epichem Ltd; the latter have also generously donated chemicals in these studies. I would also like to express my thanks to Dr. G. P. Smith and Professor J. Pola for helpful correspondence about their own work.

---

[101] J. B. Jeffries and G. P. Smith, *J. Phys. Chem.*, 1986, **90**, 487; G. P. Smith, *Int. J. Chem. Kinet.*, 1987, **19**, 269.