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Oxygen abstraction by laser pyrolysis of $W(CO)_6$; a mild route to gas-phase carbene chemistry

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SF_6-photosensitised IR laser pyrolysis of $W(CO)_6$ in the gas phase at moderate temperatures leads to unsaturated $W(CO)_n$ (n < 6) species; these prove to be effective abstractors of O atoms from a range of organic substrates, and afford a simple, clean and low-energy route from carbonyl compounds into gas phase carbene chemistry.

IR Laser Powered Homogeneous Pyrolysis (LPHP)[1,2] has been successfully exploited for over 20 years in the investigation of the mechanisms of thermal decomposition of volatile organometallic[3] and organic compounds.[4] In IR LPHP, the vapour of the target species is mixed with SF_6, and the mixture exposed to the output of a CO_2 IR laser.[2] The SF_6 strongly absorbs the laser energy, which is rapidly converted to heat *via* efficient intra- and intermolecular relaxation. The advantages of this technique are well documented; very small quantities of material are required, initiation of reaction is unambiguously homogeneous, and short-lived intermediates are readily trapped (physically or chemically). Progress of reaction may be monitored, and products quantified, by conventional analytical techniques, in the present work FTIR spectroscopy or GC–MS. The pyrolysis of many oxygenated organic compounds has been studied using IR LPHP, principally by Pola and coworkers.[5]

LPHP of $W(CO)_6$ at much lower laser powers (*i.e.* temperatures) than those required for the organic compounds described below leads to copious amounts of CO and a grey deposit, shown elsewhere to be more or less pure tungsten.[6] It is generally assumed that these products result from the successive homolytic loss of carbonyl groups. We have recently shown that in the presence of vapours of chlorinated organic compounds,[7] the deposits also contain chlorine; XPES and reflectance IR spectroscopy indicate a composition approximating to $W(CO)_4Cl_2$. It appears, therefore, that unsaturated $W(CO)_n$ (n < 6) species are highly efficient abstractors of Cl from such compounds. Moreover, the secondary product of the $W(CO)_6$, namely CO, is chemically inert, and highly reactive Cl atoms are effectively removed from the system. These factors lead to end products that may be ascribed unambiguously to subsequent reactions of the resultant C-centred radicals. In the present communication, we report preliminary results that clearly indicate that $W(CO)_n$ species are also efficient abstractors of O from C=O groups, opening a similarly mild, efficient and simple route to gas-phase carbene chemistry.

Pyrolysis (either by conventional methods or LPHP) of the simple exemplar acetone alone yields cleanly methane, ketene and ethane *via* a very well studied route that serves as a paradigm of the classic Rice–Herzfeld radical mechanism.[8] For the benchmark experiments described here, the conditions used were 2 Torr of acetone and 10 Torr of SF_6, with a laser power of approximately 8 W. By contrast, co-pyrolysis of acetone together with the room-temperature vapour pressure of $W(CO)_6$ at laser powers (*i.e.* effective temperatures) much lower than those required for decomposition of acetone alone (approximately 2 W) yielded no trace of ketene and very little methane. Instead, the major products detectable by FTIR and GC–MS in this system are higher hydrocarbons, including propane (outside the range of the GC–MS trace shown in Fig. 1), propene and 2,3-dimethylbut-2-ene in a ratio of 30 : 15 : 1, readily interpreted as the results of hydrogen abstraction reactions, a 1,2-hydrogen shift and dimerisation of dimethylcarbene, respectively. Products of other routes, such as 2-methylpropene and isomers of C_6H_{10}, are also observed. While the latter is readily interpreted as the products of H-abstraction from 2,3-dimethylbut-2-ene, the mechanism of formation of the former is not clear at this stage. Relevant portions of the total ion chromatogram trace and mass spectrum are illustrated in Fig. 1. By the same token, acetaldehyde alone thermally decomposes to yield methane and carbon monoxide,[9] whereas co-pyrolysis with $W(CO)_6$ leads to ethylene and the stereoisomers of but-2-ene (ratio 1.5 : 1). Finally, we have investigated cyclopentanone, the subject of a number of recent investigations, including O atom abstraction.[10] In the presence of $W(CO)_6$, the products are cyclopentene alone, with no trace of the allene generated *via* the more exothermic abstraction of O with C atoms.[10]

It is well known that carbenes react *via* a number of routes, including recombination, insertion into C–H or other bonds (either intra- or intermolecular), or addition across double bonds.[11] The most characteristic reaction of carbenes bearing β-

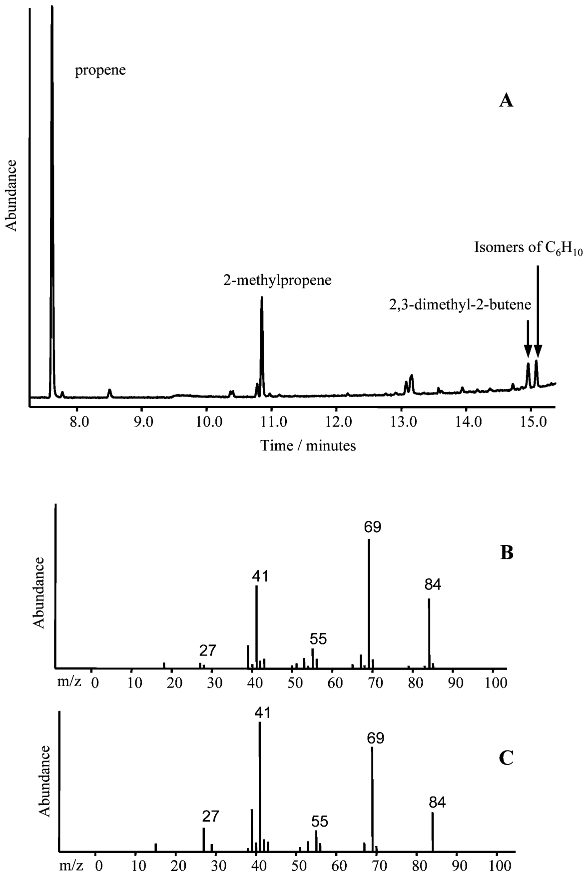

Fig. 1 Partial gas chromatogram, A, of the products of laser pyrolysis of acetone in the presence of $W(CO)_6$, and mass spectra (observed, B, and library, C) of the peak assigned to 2,3-dimethyl-2-butene.

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hydrogens is effectively a very rapid internal 1,2-hydrogen shift. Many workers have investigated this route both experimentally and computationally, with the conclusion that for simple carbenes, the activation energy for the intramolecular reaction is very low,[12] with measurements and calculations suggesting barriers of the order of 10–20 kJ mol^{-1} for dimethylcarbene. Measurements or calculations for bimolecular reactions are more limited, although reports of dimerisations for carbenes where the hydrogen shift reaction is precluded (CF_2, CCl_2 or Ar_2C, for example) support the intuitive view of a zero barrier to recombination.[13] Of course, it is quite feasible that generation of the dimerisation product involves less direct pathways, for example insertion of the carbene into the C=O bond of acetone followed by abstraction of the epoxy O atom, or addition of the carbene to propene together with a hydrogen shift. It should prove possible to distinguish these possibilities by the planned measurements of reaction rates as a function of pressures of reagents. In addition, carbenes produced *via* highly energetic routes sometimes reveal unusual fragmentation patterns involving cleavage of two bonds β to the carbene centre.[10]

Abstraction of oxygen from carbonyls is not novel, of course, and there have been many reports of studies of the resultant carbene reactions; however, the most widely used abstractors, namely metal or C atoms, generally produce carbenes of sufficient excess energy to result in atypical reaction routes.[10,14] The majority of experimental studies have utilised the photolysis of diazirines or similar compounds, and this route is also likely to produce carbenes with very substantial excess internal energies. This, together with relatively low yield, leads to domination of the unimolecular rearrangement route where available, and a consequent reduction in bimolecular products. In our system, the abstraction of O atoms by $W(CO)_n$ is likely to be marginally exothermic, if at all; the W=O bond strength is estimated at 577 kJ mol^{-1}, whereas a value of 670 kJ mol^{-1} has been reported for the C=O bond in acetone.[15] As a result, bimolecular routes become competitive with the more commonly observed unimolecular pathway. Additional features not readily probed by current experimental arrangements are the roles played by spin states or transient tungsten–carbene complexes; while the prototype CH_2 has a triplet ground state, for most higher carbenes the singlet state lies lower in energy. These aspects are more readily explored through the high-level calculations also planned.

We have also carried out similar preliminary studies of other oxygen-containing compounds. Co-pyrolysis of $W(CO)_6$ and methyloxirane (propylene oxide), for example, leads to propene, with only trace amounts of other products. In future work, we shall investigate further the mechanism of this kind of reaction, as well as bringing to bear other analytical techniques, such as matrix isolation IR spectroscopy and direct detection of short-lived intermediates in the gas phase using tunable diode laser spectroscopy.[16]

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Notes and references

1 W. M. Shaub and S. H. Bauer, *Int. J. Chem. Kinet.*, 1975, **7**, 509.

2 D. K. Russell, *Chem. Soc. Rev.*, 1990, **19**, 407; D. K. Russell, *Chem. Vap. Deposition*, 1996, **2**, 223.

3 A. S. Grady, R. D. Markwell and D. K. Russell, *Chem. Commun.*, 1991, 929; R. E. Linney and D. K. Russell, *J. Mater. Chem.*, 1993, **3**, 587; D. K. Russell, I. M. T. Davidson, A. M. Ellis, G. P. Mills, M. Pennington, I. M. Povey, J. B. Raynor, S. Saydam and A. D. Workman, *Organometallics*, 1995, **14**, 3717.

4 H. Hettema, N. R. Hore, N. D. Renner and D. K. Russell, *Aust. J. Chem.*, 1997, **50**, 363; N. R. Hore and D. K. Russell, *J. Chem. Soc., Perkin Trans. 2*, 1998, 269.

5 J. Pola, *Spectrochim. Acta., Part A*, 1990, **46**, 607.

6 K. E. Lewis, D. M. Golden and G. P. Smith, *J. Am. Chem. Soc.*, 1986, **106**, 3905.

7 G. R. Allen, N. D. Renner and D. K. Russell, *Chem. Commun.*, 1998, 703.

8 F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 1934, **56**, 284; J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, 1955, **77**, 4719; J. Pola, J. Vitek, M. Horak and P. Engst, *Collect. Czech. Chem. Commun.*, 1980, **45**, 1805; S. H. Mousavipour and P. D. Pacey, *J. Phys. Chem.*, 1996, **100**, 3573; R.-H. Li, J.-C. Wu, J.-L. Chang and Y.-T. Chen, *Chem. Phys.*, 2001, **274**, 275.

9 K. J. Laidler and M. T. H. Liu, *Proc. R. Soc. London, Ser. A*, 1967, **297**, 365; M. T. H. Liu and K. J. Laidler, *Can. J. Chem.*, 1968, **46**, 479.

10 G. Xu, T.-M. Chang, J. Zhou, M. L. McKee and P. B. Shevlin, *J. Am. Chem. Soc.*, 1999, **121**, 7150 and references therein.

11 W. Kirmse, *Carbene Chemistry*, Academic Press, New York, 2nd edn., 1971; W. J. Baron, M. R. DeCamp, M. Jones Jr., R. H. Levin and M. B. Sohn, in *Carbenes*, ed. M. Jones Jr. and R. A. Moss, Wiley & Sons, New York, 1973, vol. 1, p. 1.

12 H. M. Frey and I. D. R. Stephens, *J. Chem. Soc*, 1963, 3514; H. Bock, G. Tschmutowa and H. P. Wolf, *J. Chem. Soc., Chem. Commun.*, 1986, 1068; D. A. Modarelli and M. S. Platz, *J. Am. Chem. Soc.*, 1991, **113**, 8985; B. Ma and H. F. Schaefer, *J. Am. Chem. Soc.*, 1994, **116**, 3539; D. M. Miller, P. R. Schreiner and H. F. Schaefer, *J. Am. Chem. Soc.*, 1995, **117**, 4137; C. A. Ricjards, S.-Y. Kim, Y. Yamaguchi and H. F. Schaefer, *J. Am. Chem. Soc.*, 1995, **117**, 10104; F. Ford, T. Yuzawa, M. S. Plarz, S. Matzinger and M. Fülscher, *J. Am. Chem. Soc.*, 1998, **120**, 4430; L. T. Eunju, Z. Zhedong, M. S. Platz, J. P. Pezacki and J. Warkentin, *J. Phys. Chem.*, 1999, **103**, 5336; G. Wu, D. Stacchiola, M. Kaltchev and W. T. Tysoe, *J. Am. Chem. Soc.*, 2000, **122**, 8232; I. R. Likhotvorik, E. Tippmann and M. S. Platz, *Tetrahedron Lett.*, 2001, **42**, 3049.

13 F. Battin-Leclerc, A. P. Smith, G. D. Hayman and T. P. Murrells, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3305; S. S. Kumaran, M.-C. Su, K. P. Lim, J. V. Michael, S. J. Klippenstein, J. DiFelice, P. S. Mudipalli, J. H. Kiefer, D. A. Dixon and K. A. Peterson, *J. Phys. Chem. A*, 1997, **101**, 8653; M. A. Smith and E. R. Ritter, *Chem. Phys. Processes Combust.*, 1999, 391; C. Suzuki, K. Sasaki and K. Kadota, *Plasma Chem. Plasma Process.*, 2001, **21**, 139; H. Tomioka, T. Watanabe, M. Hattori, N. Nomura and K. Hirai, *J. Am. Chem. Soc.*, 2002, **124**, 474.

14 P. S. Skell and J. H. Plonka, *Tetrahedron*, 1972, **28**, 3571; K. Liu and J. M. Parson, *J. Phys. Chem.*, 1979, **83**, 970; A. P. Bell and A. G. Wedd, *J. Organomet. Chem.*, 1979, **181**, 81; T. P. Blatchford, M. H. Chisholm, K. Folting and J. C. Huffman, *Gov. Rep. Announce. Index*, 1985, **85**, 59; M. Rahman and P. B. Shevlin, *Tetrahedron Lett.*, 1985, **26**, 2959; D. G. Kovacs, *Diss. Abstr. Int. B*, 1999, **60**, 1089; C. Bozkurt, *J. Organomet. Chem.*, 2000, **603**, 252.

15 J. C. Bryan and J. M. Mayer, *J. Am. Chem. Soc.*, 1990, **112**, 2298; *CRC Handbook of Physics and Chemistry*, ed. R. C. Weast, CRC Press Inc., Roca Baton, Fl., 60th edn., 1979, p. F220.

16 D. K. Russell and R. Wesendrup, *J. Chem. Phys*, 2002, in press.