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

Grant R. Allen, Noel D. Renner and Douglas K. Russell*†

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

SF_6-photosensitised IR laser pyrolysis of $W(CO)_6$ in the gas phase at moderate temperatures leads to unsaturated $W(CO)_n$ species; these prove to be very effective and selective abstractors of Cl atoms from a wide range of organic substrates, and offer a low energy and clean route into gas phase organic radical 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. The SF_6 strongly absorbs the laser energy, which is rapidly converted to heat *via* efficient intra- and inter-molecular relaxation.[2] 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 by conventional analytical techniques, in the present work FTIR spectroscopy or GC–MS. The pyrolysis of many organochlorine compounds has been studied using IR LPHP, principally by Pola.[5] As in conventional pyrolysis, the chemistry of these compounds is dominated by the themes of HCl elimination (where available) and C–Cl bond homolysis.

LPHP of $W(CO)_6$ at much lower laser powers (*i.e.*, temperatures) than those required for the organochlorine 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 usually assumed that these products result from the successive homolytic loss of carbonyl groups. In the presence of vapours of chlorinated organic compounds, the deposits also contain chlorine, XPES and reflectance IR spectroscopy indicating 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. Where the target compound contains both Cl and F, abstraction of Cl occurs preferentially, in accord with the relative strengths of W–X and C–X bonds.[7] 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 organic radicals. Here, we report preliminary results using simple and familiar systems which confirm this point of view, and which illustrate the potential of this route into gas phase organic radical chemistry.

The thermal decomposition of the refrigerant CF_2HCl (Freon 22) has been extensively studied by both conventional methods and IR LPHP in the light of its role in destruction of stratospheric ozone.[1,8] In all cases, the observed products were HCl and C_2F_4, with further breakdown of the latter at higher temperatures. This has been ascribed to unimolecular elimination of HCl followed by recombination of the resultant difluorocarbene $:CF_2$. In the present work, the $:CF_2$ intermediate was detected directly by IR spectroscopy in an Ar matrix (dilution 100 : 1). At 15 K, a strong peak at 1220 cm^{-1} attributable to CF_2 was observed; on annealing to 40 K, this peak decayed, to be replaced by two assignable to C_2F_4 at 1178 and 1328 cm^{-1}. On co-pyrolysis with $W(CO)_6$ at much lower laser power (*i.e.*, temperature), the major products were SiF_4 and 1,1,2,2-tetrafluoroethane; no traces of HCl or C_2F_4 (or its breakdown products) were detected. These results are consistent with the selective abstraction of Cl to yield the $\cdot CF_2H$ radical; this either recombines or migrates to the cell wall, where reaction with silica results in the observed SiF_4. The decomposition of CF_2Cl_2 (Freon 12) and CH_2Cl_2 led to corresponding results, in particular the production of 1,2-dichlorotetrafluoroethane in copyrolysis of the former, and of 1,2-dichloroethane in the latter. Neither of these compounds is a major product in conventional pyrolysis, as a result of competing elimination processes and extensive secondary reactions.

The series of halogenated acetic acids provides an interesting example of a change in pyrolysis mechanism down a series.[9] Decarbonylation of the intermediate oxiranone formed by elimination of HCl from CH_2ClCO_2H yields formaldehyde, CO and HCl as the observed end products. On the other hand, C–I homolysis in CH_2ICO_2H, followed by a hydrogen shift and decarboxylation, results in CH_4 and CO_2 as the stable products; CH_2BrCO_2H follows both routes concurrently. On co-pyrolysis with $W(CO)_6$ at very low temperatures, CH_2ClCO_2H also yields the radical abstraction end-products CH_4 and CO_2. Similarly, IR LPHP of CH_3COCl alone largely follows the HCl elimination pathway, yielding the ketene observed in conventional pyrolysis.[10] Low temperature co-pyrolysis with $W(CO)_6$ completely suppresses formation of ketene, resulting instead in the CH_4 and CO characteristic of the radical route. These results are illustrated in Fig. 1.

The IR LPHP of 1,2-dichloroethene has been studied by Kubat and Pola,[11] with the conclusion that pyrolysis at low temperature leads to *Z*–*E* isomerisation; at higher laser power, this is followed by elimination of HCl yielding chloroacetylene (and, to a small extent, of Cl_2 to yield acetylene). In the present work, a sample of the slightly less stable *E*-1,2-$C_2H_2Cl_2$ alone was initially exposed to low laser power to yield an approximately equimolar mixture of the *Z* and *E* isomers. $W(CO)_6$ was then admitted to the cell, and further IR LPHP at powers insufficient to lead to further isomerisation led to decay of IR features of the two isomers at different rates. The first-order kinetic plots of Fig. 2 are consistent with reactions whose

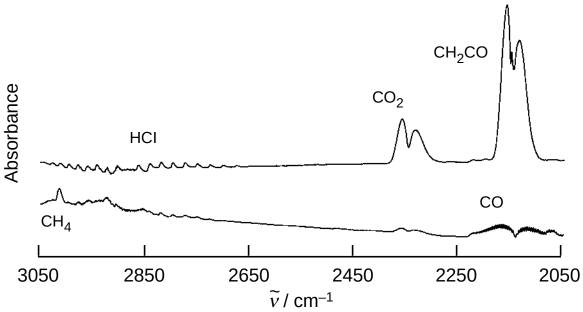

Fig. 1 Partial FTIR spectra of the products of laser pyrolysis of CH_3COCl in the absence (upper) and presence (lower) of $W(CO)_6$; the small amount of HCl evident in the lower trace was present in the original sample

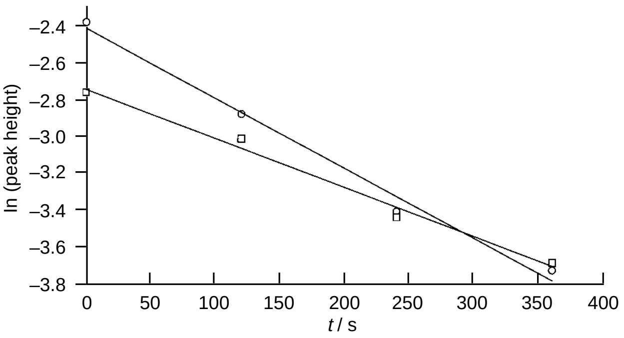

Fig. 2 First-order kinetic plots for the decay of *E*-1,2-$C_2H_2Cl_2$ (○) and *Z*-1,2-$C_2H_2Cl_2$ (□) on laser pyrolysis in the presence of $W(CO)_6$

activation energies differ by the known zero point energy difference[12] of 1840 J mol^{-1}, and an effective temperature of 650 ± 150 K. This 'kinetic isomer effect' suggests that loss reactions of the two isomers involve Cl abstraction pathways whose transition states differ little in energy.

The above preliminary results confirm that $W(CO)_n$ species do indeed act as efficient and selective abstractors of Cl from a range of organochlorine compounds under comparatively mild conditions, and that the subsequent chemistry is dominated by the resulting organic radical species. In this sense, this system may serve as a gas phase analogue of well known solution abstractors such as tri-*n*-butyltin[13] and tris(trimethylsilyl)silyl.[14] In future work, we shall investigate more complex systems; preliminary results on chlorinated xylenes, for example, have already indicated that substantially new reaction routes are opened in such species.[15]

We thank the University of Auckland for assistance with the purchase of equipment and a doctoral scholarship to G. R. A.

Notes and References

† E-mail: d.russell@auckland.ac.nz

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; *Chem. Vap. Deposition*, 1996, **2**, 223.
3 A. S. Grady, R. D. Markwell and D. K. Russell, *J. Chem. Soc., 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 *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press Inc., Roca Baton, FL, 60th edn., 1979, p. F220.
8 S. S. Kumaran, K. P. Lim, J. V. Michael, M. C. Su and A. F. Wagner, *J. Phys. Chem.*, 1996, **100**, 15827 and references therein.
9 H. Hettema, N. R. Hore, N. D. Renner and D. K. Russell, *Aust. J. Chem.*, 1997, **50**, 363.
10 H. Bock, T. Hirabayashi, S. Mohmand and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 105; V. R. Stimson and J. W. Tilley, *Aust. J. Chem.*, 1977, **30**, 81.
11 P. Kubat and J. Pola, *Z. Phys. Chem.*, 1987, **268**, 849.
12 N. C. Craig, L. G. Piper and V. L. Wheeler, *J. Phys. Chem.*, 1971, **75**, 1453.
13 W. P. Neumann, *Synthesis*, 1987, 665.
14 C. Chatgilialoglu, *Acc. Chem. Res.*, 1992, **25**, 188.
15 G. R. Allen and D. K. Russell, unpublished work.

Received in Exeter, UK, 4th December 1997; 7/08737C