this iron(II) porphyrin and the vinylidene carbene derived from DDT.

We are currently looking for the occurrence of such a carbene complex during reductive metabolization of DDT by microsomal cytochrome P 450 and studying the chemical properties of complex **1**.

References and notes

(1) Used abbreviations: DDT = 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane; TPP = the dianion of *meso*-tetraphenylporphyrin; DDD = 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane; *p*-methyl- (or chloro-) TPP = the dianion of *meso*-tetra-*p*-methyl- (or chloro-) phenylporphyrin.

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(10) The ortho protons of the TPP phenyl rings appear as a broad signal centered around 8 ppm at 34 °C (90 MHz, Varian EM 390). At −30 °C (250 MHz, Cameca), they appear as two signals at 8.11 and 7.63 ppm. This is due to the rotation of the TPP phenyl rings which is slow, on the NMR time scale at −30 °C, and which gives a coalescence of the signals at 34 °C.

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(12) We could not detect the ^{13}C NMR signal (Bruker WH 90, sweep width 6000 Hz, 11 000 45° pulses, 8K points memory blocks, acquisition time 0.67 s) of the carbon bound to the iron, even with a CDCl$_3$ solution saturated with complex **1** ($\simeq 2 \times 10^{-2}$ M). This could be expected for such a quaternary carbon far from any proton. Accordingly, ^{13}C enrichment has been necessary to find the location of the corresponding carbene carbon in the TPP–Fe(CCl$_2$) complex.^{6}

(13) Upon heating the sample (Varian CH7 mass spectrometer), a spectrum, corresponding to (Cl—C$_6$H$_4$)$_2$C=C, appears suddenly at ~70 °C; this is certainly due to the thermal decomposition of complex **1**. No peaks corresponding to the porphyrin moiety are observable at this temperature.

(14) Such a stability is only obtained with thoroughly purified complex **1**.

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Very Low Pressure Reactor. A New Technique for Measuring Rates and Equilibria of Radical–Molecule Reactions at Low Temperature. Heat of Formation of the Methyl Radical[1a]

Sir:

We wish to report here a new method for measuring rate constants and equilibrium constants of molecule–radical reactions near ambient temperatures. The method, using a very low pressure reactor (VLPR) is a variation of our very low pressure pyrolysis technique (VLPP) which has been described in detail elsewhere.[2] VLPP has been restricted to high temperatures (>700 K) because of the necessity of generating radicals rapidly (<10^{-1} s) via thermal pyrolysis. It also suffers from the difficulty of requiring extensive correction for radical reactions on the reactor walls. We have solved the first problem of generating radicals at low temperatures by dissociating diatomics in a microwave discharge and diffusing them into the reactor. The atoms as generated will react with suitably chosen substrates to form radicals. The surface reactivity problem has been solved by using a fluorocarbon coating on our reactor walls which seems to be totally inert (<10^5 collisions) to reactive atoms or radicals.[3] We are engaged in an extensive study

of radical reactions using these technique. The present report is concerned with its application to equilibria.

Gas phase equilibrium data for radical reactions at room temperature represent the most direct route to the thermochemistry of free radicals. Present values for the enthalpies of formation of free radicals are known, at best, to within 1 kcal/mol and therefore rather crude values of equilibrium constants, even with a 50% error, will reduce this uncertainty to 0.25 kcal/mol, that is to the level of accuracy of the reported $\Delta H_f°$'s for hydrocarbons.

The experimental determination of k at room temperature, however, is not straightforward for several reasons. First, and most important, it is necessary to generate thermally an appreciable concentration of radicals and, second, to prevent them from taking part in spurious reactions.

The high reactivity of chlorine atoms toward hydrocarbons has allowed us to overcome the first difficulty. By working at very low pressure, we eliminated the second one.

In this communication we describe a study of the equilibrium

$$Cl + CH_4 \underset{-1}{\overset{1}{\rightleftharpoons}} HCl + CH_3 \qquad (1)$$
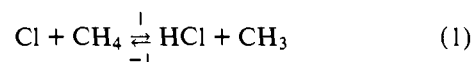
under very low pressure conditions.

The apparatus described lends itself quite generally to the quantitative study of atom–molecule, radical–molecule, and radical–radical reactions in the temperature range −80 to 150 °C, the upper limit being provided by the melting point of the waxes used to cover the glass surfaces.

Chlorine atoms were produced by microwave discharge of a mixture of <1% Cl$_2$ in He in a discharge tube previously treated with H$_3$PO$_4$ and leaked into the reactor through a pinhole (~100 μ). CH$_4$ and/or HCl could be introduced via a second capillary inlet at variable flow rates. The reactor, similar to those described elsewhere,[2] had a 1-mm exit aperture and was coated with a film of halocarbon wax to prevent atom recombination.[3a]

The reaction mixture was analyzed by a modulated beam mass spectrometer whose design and mode of operation have been previously described.[2c] Some experimental points deserve comment: (1) the condition [CH$_4$] >> [Cl] was maintained in most experiments; (2) molecular chlorine could be completely dissociated in the discharge tube and no appreciable recombination took place inside the reactor;[4a] (3) the products of the equilibrium reactions (1, −1) were the only ones detected. No CH$_3$Cl was ever found. The steady-state kinetic equations for the forward reaction (1) is

$$R_{Cl} = k_1[Cl][CH_4] + k_{eCl}[Cl] = k_{eCl}[Cl]_0$$

$$[Cl]_0/[Cl] = 1 + k_1[CH_4]/k_{eCl} \qquad (2)$$

where k_{ex} is the unimolecular escape rate constant for the species x[4c] and R_{Cl} the incoming flow of chlorine atoms in molecules/(cm^3 s). If the back reaction (−1) makes negligible contributions to the kinetics, then a plot of [Cl]$_0$/[Cl] vs. [CH$_4$] would yield a value of k_1.

When HCl is also added to the reaction mixture, the following equations apply,

$$k_{eCl}[Cl]_0 = k_{eCl}[Cl] + k_1[CH_4][Cl] - k_{-1}[CH_3][HCl]$$

$$k_1[CH_4][Cl] - k_{-1}[CH_3][HCl] - k_{eCH_3}[CH_3] = 0$$

which upon rearrangement give

$$\frac{[Cl]}{[Cl]_0 - [Cl]} = \frac{k_{eCl}}{k_1[CH_4]} + \frac{k_{-1}}{k_1}\left(\frac{k_{eCl}}{k_{eCH_3}}\right)\left(\frac{[HCl]}{[CH_4]}\right) \qquad (3)$$

At constant [CH$_4$], [Cl]/([Cl]$_0$ − [Cl]) becomes a linear function of [HCl]. Plotting [Cl]/[Cl]$_0$ − [Cl] against [HCl]/[CH$_4$] gives a straight line whose slope = 0.654 k_{-1}/k_1 = 0.654/K_1.[4c]

Table I. Thermochemical Data at 298 K[a]

Species	$\Delta H°_f$, kcal/mol	$S°$, gibbs/mol
CH_4	-17.9	44.5
CH_3	34.9 ± 0.15^b	46.4 ± 0.3
Cl	28.9	39.5
HCl	-22.0	44.6

[a] Reference 10. [b] Present work.

The forward reaction (1) has been extensively investigated[3c,4b,5,6,7] in the last few years and our value of $k_1 = 0.93$ (± 0.05) $\times 10^{-13}$ cm^3/(molecule s) is in excellent agreement with those[8,9] studies lending additional support to our measurements. In addition, systematic errors will tend to cancel out when the ratio of k_1/k_{-1} is calculated and therefore we consider that K_1 has been determined with considerable accuracy; $K_1(298$ K$) = 1.3 \pm 0.3$. This result, in conjunction with thermochemical data for reactions 1, -1 (Table I) leads to $\Delta H°_f(CH_3) = 34.9 \pm 0.15$ and BDE (CH$_3$–H) $= 104.9 \pm 0.15$ kcal/mol, in very good agreement with literature values.[11]

To the best of our knowledge, this represents the first time the equilibrium constant for a chemical reaction involving a very reactive organic free radical has ever been measured directly.[12]

References and Notes

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On the Structure of Starch–Iodine

Sir:

It has been known for many years that the linear, helical component of starch, amylose, forms an intensely blue-black adduct with iodine in the presence of iodide.[1] The pioneering spectral and x-ray diffraction investigations of Rundle and co-workers[2] established that the iodine atoms are present in a one-dimensional chain within the amylose helix (arrayed in a periodicity probably incommensurate with the pitch of the helix) and give rise to the intense optical absorption ($\lambda_{max} \approx 600$ nm).[2] The exact structural nature of the polyiodide chromophore has been the subject of considerable study and speculation. For example, it has been proposed that the iodine is present as discrete I$_2$ units,[3a] "dissolved" in the hydrophobic interior of the helix,[1b,3b] and also that iodine is present as linear chains of I$_3^{-1}$ (A) ions as in (benzamide)$_2$ H$^+$I$_3^-$.[4] In addition,
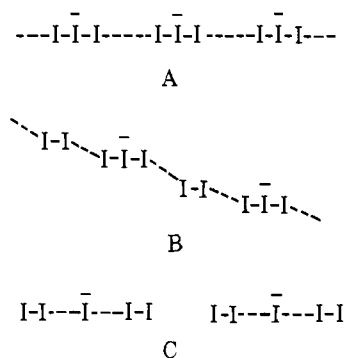
studies of related cyclohexaamylose complexes[5] suggest the possibility of arrays of alternating I$_2$ and I$_3^-$ units (B) or symmetrical I$_5^-$ species (C). Despite the application of a variety of physical techniques to this problem,[6] it has not been possible to differentiate among these structures and to provide definitive information on the identity of the polyiodide species present in starch–iodine. We have recently shown that the combination of resonance Raman[7] and iodine-129 Mössbauer spectroscopy,[8] aided by studies of appropriately selected model compounds, is a powerful tool for elucidating polyiodide structure in low-dimensional mixed valence materials.[9] In this communication we apply these techniques to the starch–iodine problem. We provide unambiguous evidence that the predominant polyiodide species within the amylose helix is I$_5^-$.

In Figure 1 are presented resonance Raman scattering spectra (5145-Å excitation, spinning samples) of the amylose–iodine complex (prepared in deionized water from potato amylose, I$_2$, and KI, washed with deionized water, and freeze dried)[10] and several key model compounds of known structure. In general, only totally symmetric normal vibrational modes (and the corresponding overtones and combinations) exhibit appreciable intensity in polyiodide resonance Raman spectra.[9] The observed I–I stretching frequencies reflect the tendency of I$_2$ to act as an electron acceptor and of electron donors (e.g., I$^-$) to lower the I–I bond order.[9a,11] Thus, coordination of I$^-$ to I$_2$ producing I$_3^-$ lowers the I–I stretching frequency from 207 to 128 cm^{-1} (the average of the Raman-active totally symmetric stretch at 108 cm^{-1} and the infrared-active antisymmetric stretch at 148 cm^{-1} [12]). As can be seen in Figure 1A, starch–iodine exhibits strong scattering at 163 cm^{-1}, and very weak scattering at 109 and 56 cm^{-1}; overtones and combinations are also observed.[13] This spectrum differs sharply from those of I$_2$ in benzene (Figure 1C, ν_{fund} 207 cm^{-1}; fund = fundamental) alcohols or ethers,[14] (benzamide)$_2$H$^+$I$_3^-$ (Figure 1D, $\nu_{I_3-symm,fund}$ 108 cm^{-1}), which has structure A,[4] and either (phenacetin)$_2$H$^+$I$_3^-\cdot$I$_2$[15a] (Figure 1E, $\nu_{"I_2"}$ 187 cm^{-1}, $\nu_{"I_3-"}$ 120 cm^{-1})[15b] or (α-cyclohexaamylose)$_2$Li$^+$I$_3^-\cdot$I$_2\cdot$8H$_2$O[5] (Figure 1F, $\nu_{"I_2"}$ 173 cm^{-1}, $\nu_{"I_3-"}$ 110 cm^{-1})[15b] which have structure B. On the other hand, compounds with chains of I$_5^-$ ions (structure C) exhibit a spectrum essentially identical with that of the starch compound. Thus, (trimesic acid$\cdot$H$_2$O)$_{10}$H$^+$I$_5^-$ [16] (Figure 1B) exhibits strong scattering at 162 cm^{-1} and weaker bands at 104 and 75 cm^{-1}.[15b] The 162-cm^{-1} transition is reasonably assigned to a fundamental