

# Communications to the Editor

## Reaction of 2,2-Bis(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT) with Iron(II) Porphyrins. Isolation of the Vinylidene Carbene Complex, Tetraphenylporphyriniron(II) (C=C(*p*-Cl-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>)

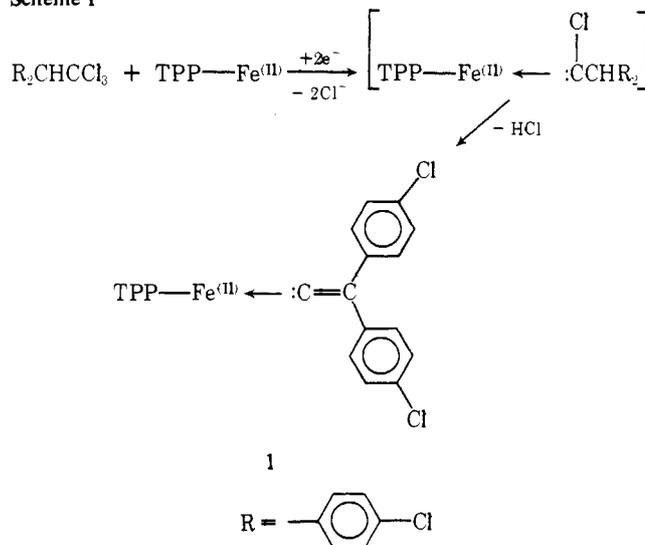
Sir:

The widely used insecticide DDT<sup>1</sup> (2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane) has been shown to interact with various metallic centers of living organisms.<sup>2</sup> Its reductive dechlorination has been demonstrated *in vivo* and *in vitro* and should involve reduced iron of hemoproteins or cobalt of vitamin B<sub>12</sub>.<sup>2</sup> Iron(II) deuteroporphyrin IX,<sup>3</sup> myoglobin, and cytochrome *c* oxidase<sup>4</sup> reduce DDT into DDD.<sup>1</sup> Moreover, a  $\sigma$ -vinylcobalt(III) complex has been isolated as a product of reaction between DDT and a cobaloxime.<sup>5</sup>

We have recently isolated a TPP-Fe<sup>II</sup>(CCl<sub>2</sub>) complex formed during reaction of TPP-Fe<sup>II</sup> with CCl<sub>4</sub> in the presence of an excess of reducing agent<sup>6</sup> and proved its carbenic structure by an x-ray analysis.<sup>7</sup> Various polyhalogenated compounds, RCX<sub>3</sub>, react similarly with iron(II) porphyrins, leading to the corresponding porphyriniron (CXR) carbenic complexes<sup>6</sup> and some evidences have been produced in favor of the formation of such carbene complexes of hepatic cytochrome P 450 iron(II) during reductive metabolization of the polyhalogenated compounds.<sup>8,9</sup> This paper shows that stable complexes are formed during reactions between DDT and iron porphyrins, in the presence of an excess of reducing agent, and describes the isolation and some properties of the complex derived from reaction of TPP-Fe<sup>II</sup> and DDT, which is the first reported vinylidene carbene complex of a metalloporphyrin. Reaction of 10<sup>-3</sup> M TPP-Fe<sup>II</sup> in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (9:1) with DDT (1.4 equiv added progressively within 3 h), in the presence of an excess of iron powder, with vigorous stirring under argon, can be followed by visible spectroscopy. After 3.5 h at 20 °C, the spectrum of TPP-Fe<sup>II</sup> is entirely replaced by that of a new species with peaks at 417 and 521 nm in benzene. After filtration of the solution, washing with water containing sodium dithionite, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH, purple crystals of complex **1** are obtained (50% yield after three recrystallizations):  $\lambda$  417 nm ( $\epsilon$  1.26  $\times$  10<sup>5</sup>), 521 (13.6  $\times$  10<sup>3</sup>), 543 (sh) in benzene.

Complex **1** is a low-spin TPP-Fe<sup>II</sup> complex as shown by its magnetic susceptibility,  $\mu_{\text{eff}} = 0^{11}$  and by the chemical shifts and shape of the NMR signals of its porphyrin hydrogens and carbons—<sup>1</sup>H NMR (CDCl<sub>3</sub>, Si(CH<sub>3</sub>)<sub>4</sub>)  $\delta$  7.75 and 8 (m, 20 H),<sup>10</sup> 8.71 ppm (s, 8 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, Si(CH<sub>3</sub>)<sub>4</sub>)  $\delta$  145.8, 141, 133, 132.2, 127.5, 126.5, 121.9—which are similar to those of the corresponding signals of TPP-Fe(CCl<sub>2</sub>).<sup>6</sup> The <sup>1</sup>H and <sup>13</sup>C NMR data concerning the porphyrin ring are indicative of an axial symmetry and the spectra exhibit only the following signals in addition to those of the porphyrin ring: <sup>1</sup>H NMR  $\delta$  6.42 (d,  $J = 9$  Hz, 4 H), 4.02 (d,  $J = 9$  Hz, 4 H); <sup>13</sup>C NMR  $\delta$  151.8, 130.3, 127.2, 125.4, 124.4 ppm.<sup>12</sup> These NMR data, together with the elemental analysis (C, H, Cl, N) of complex **1**, which is in agreement with the formula C<sub>58</sub>H<sub>36</sub>Cl<sub>2</sub>FeN<sub>4</sub> of TPP-Fe[C=C(C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub>], and with its mass spectrum (70 eV),<sup>13</sup> which exhibits an intense peak with an isotopic cluster characteristic of the presence of two chlorine atoms at  $m/e$  246 (for <sup>35</sup>Cl), are indicative of the vinylidene (*p*-Cl-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=C ligand. All of these data for complex **1**

Scheme I



are in agreement with those of a pentacoordinated TPP-Fe<sup>II</sup> complex with the C=C(C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub> ligand.

Like TPP-Fe(CCl<sub>2</sub>),<sup>6</sup> complex **1** is able to bind various ligands (L) in the position trans to the carbene and is thus in equilibrium in solution with the corresponding hexacoordinated complexes: L = CH<sub>3</sub>OH, formation constant at 25 °C  $K = 6$  L mol<sup>-1</sup>,  $\lambda$  427 nm ( $\epsilon$  2  $\times$  10<sup>5</sup>) and 535 (13  $\times$  10<sup>3</sup>); L = pyridine,  $K = 3300$ ,  $\lambda$  428 nm ( $\epsilon$  2  $\times$  10<sup>5</sup>), 505 (sh), and 542 (10.5  $\times$  10<sup>3</sup>); L = *N*-methylimidazole,  $K = 75$  000,  $\lambda$  430 nm ( $\epsilon$  2  $\times$  10<sup>5</sup>), 505 (sh), and 545 (11.5  $\times$  10<sup>3</sup>). In the presence of a large excess of pyridine, the hexacoordinated complex, TPP-Fe[C=C(C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub>](pyridine) is slowly transformed into TPP-Fe<sup>II</sup>(pyridine)<sub>2</sub>, the reaction between the iron complex (7  $\times$  10<sup>-5</sup> M) and 1 M pyridine being complete after 5 h at 27 °C. The main difference between complex **1** and its hexacoordinated derivatives on one hand, and the carbene complex TPP-Fe(CCl<sub>2</sub>) on the other hand, is the remarkable stability of the former toward oxidation in aerated solvents. For instance, complex **1** remains unchanged several days in aerated benzene,<sup>14</sup> though TPP-Fe(CCl<sub>2</sub>) has a half-life of 4 h under the same conditions.<sup>6</sup>

Formation of complex **1** from DDT involves, like the formation of TPP-Fe(CCl<sub>2</sub>) from CCl<sub>4</sub>,<sup>6</sup> the reductolysis of two C-Cl bonds of the starting polyhalogenated compound (Scheme I). In the case of DDT, a  $\beta$  elimination of HCl can then occur leading to the vinylidene carbene. Such an elimination has been reported in the reaction of DDT with cobalamincobalt(I)<sup>5</sup> leading to the formation of a  $\sigma$ -vinyl cobalt(III) complex.

Vinylidene carbene complexes similar to **1** are formed by reaction of DDT with various iron(II) porphyrins, in the presence of an excess of reducing agent. As for TPP-Fe<sup>II</sup>, the visible spectra obtained after reactions of DDT with various iron(II) porphyrins (*p*-methyl-TPP, *p*-chloro-TPP, octaethylporphyrin, and protoporphyrin IX) are similar to those obtained after reactions of these iron(II) porphyrins with CCl<sub>4</sub>.<sup>7</sup> Thus, the new spectrum which has been observed after reaction of DDT with a porphyrin bound to an undecapeptide derived from cytochrome *c*, in the presence of excess sodium dithionite,<sup>4</sup> should correspond to the complex formed between

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 metabolism 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.
- (2) D. A. Stotter, *J. Inorg. Nucl. Chem.*, **39**, 721 (1977).
- (3) (a) C. E. Castro, *J. Am. Chem. Soc.*, **86**, 2310 (1964); (b) R. S. Wade and C. E. Castro, *ibid.*, **95**, 226 (1973).
- (4) D. A. Stotter, R. D. Thomas, and M. T. Wilson, *Bioinorg. Chem.*, **7**, 87 (1977).
- (5) (a) R. H. Prince, G. M. Sheldrick, D. A. Stotter, and R. Taylor, *J. Chem. Soc., Chem. Comm.*, 854 (1974); (b) D. A. Stotter, G. M. Sheldrick, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 2124 (1975).
- (6) D. Mansuy, M. Lange, J. C. Chottard, P. Guerin, P. Morlière, D. Brault, and M. Rougee, *J. Chem. Soc., Chem. Commun.*, 648, (1977).
- (7) D. Mansuy, M. Lange, J. C. Chottard, J. F. Bartoli, B. Chevlier, and R. Weiss, unpublished work.
- (8) D. Mansuy, W. Nastainczyk, and V. Ullrich, *Arch. Pharmakol.*, **285**, 315 (1974).
- (9) C. R. Wolf, D. Mansuy, W. Nastainczyk, G. Deutschmann, and V. Ullrich, *Mol. Pharmacol.*, **13**, 698 (1977).
- (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.
- (11) Measured by the Evans' method: D. F. Evans, *Chem. Commun.*, 2003 (1959).
- (12) We could not detect the <sup>13</sup>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 CCl<sub>4</sub> solution saturated with complex 1 (≈ 2 × 10<sup>-2</sup> M). This could be expected for such a quaternary carbon far from any proton. Accordingly, <sup>13</sup>C enrichment has been necessary to find the location of the corresponding carbene carbon in the TPP-Fe(CCl<sub>2</sub>) complex.<sup>6</sup>
- (13) Upon heating the sample (Varian CH7 mass spectrometer), a spectrum, corresponding to (Cl-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>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<sup>1a</sup>

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.<sup>2</sup> VLPP has been restricted to high temperatures (>700 K) because of the necessity of generating radicals rapidly (<10<sup>-1</sup> 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 substitutes 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<sup>5</sup> collisions) to reactive atoms or radicals.<sup>3</sup> We are engaged in an extensive study

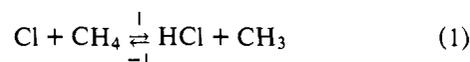
of radical reactions using these technique. The present report is concerned with its application to equilibria.

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  $\Delta H_f^\circ$ '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



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<sub>2</sub> in He in a discharge tube previously treated with H<sub>3</sub>PO<sub>4</sub> and leaked into the reactor through a pinhole (~100 μ). CH<sub>4</sub> and/or HCl could be introduced via a second capillary inlet at variable flow rates. The reactor, similar to those described elsewhere,<sup>2</sup> had a 1-mm exit aperture and was coated with a film of halocarbon wax to prevent atom recombination.<sup>3a</sup>

The reaction mixture was analyzed by a modulated beam mass spectrometer whose design and mode of operation have been previously described.<sup>2c</sup> Some experimental points deserve comment: (1) the condition [CH<sub>4</sub>] ≫ [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;<sup>4a</sup> (3) the products of the equilibrium reactions (1, -1) were the only ones detected. No CH<sub>3</sub>Cl was ever found. The steady-state kinetic equations for the forward reaction (1) is

$$R_{\text{Cl}} = k_1[\text{Cl}][\text{CH}_4] + k_{\text{eCl}}[\text{Cl}] = k_{\text{eCl}}[\text{Cl}]_0$$

$$[\text{Cl}]_0/[\text{Cl}] = 1 + k_1[\text{CH}_4]/k_{\text{eCl}} \quad (2)$$

where *k<sub>ex</sub>* is the unimolecular escape rate constant for the species *x*<sup>4c</sup> and *R<sub>Cl</sub>* the incoming flow of chlorine atoms in molecules/(cm<sup>3</sup> s). If the back reaction (-1) makes negligible contributions to the kinetics, then a plot of [Cl]<sub>0</sub>/[Cl] vs. [CH<sub>4</sub>] would yield a value of *k<sub>1</sub>*.

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

$$k_{\text{eCl}}[\text{Cl}]_0 = k_{\text{eCl}}[\text{Cl}] + k_1[\text{CH}_4][\text{Cl}] - k_{-1}[\text{CH}_3][\text{HCl}]$$

$$k_1[\text{CH}_4][\text{Cl}] - k_{-1}[\text{CH}_3][\text{HCl}] - k_{\text{eCH}_3}[\text{CH}_3] = 0$$

which upon rearrangement give

$$\frac{[\text{Cl}]}{[\text{Cl}]_0 - [\text{Cl}]} = \frac{k_{\text{eCl}}}{k_1[\text{CH}_4]} + \frac{k_{-1}}{k_1} \left( \frac{k_{\text{eCl}}}{k_{\text{eCH}_3}} \right) \left( \frac{[\text{HCl}]}{[\text{CH}_4]} \right) \quad (3)$$

At constant [CH<sub>4</sub>], [Cl]/([Cl]<sub>0</sub> - [Cl]) becomes a linear function of [HCl]. Plotting [Cl]/([Cl]<sub>0</sub> - [Cl]) against [HCl]/[CH<sub>4</sub>] gives a straight line whose slope = 0.654 *k<sub>-1</sub>*/*k<sub>1</sub>* = 0.654/*K<sub>1</sub>*.<sup>4c</sup>