An E.S.R. Study of the Trimethyl Phosphate Radical Cation–Trichlorofluoromethane σ* Complex and Its Dissociation

Xue-Zhi Qin,† Brian W. Walther, and Ffrancon Williams*

*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996–1600, U.S.A.*

The radical cation generated radiolytically at 77 K in a trimethyl phosphate–$CFCl_3$ solid solution is a σ* complex which undergoes a hydrogen atom rearrangement upon thermal or photoinduced dissociation.

Recently, solvent hyperfine interactions have been observed for a small number of radical cations generated radiolytically in Freon matrices.[1—4] The methyl formate cation has aroused particular interest since it forms a strong σ* complex with a $CFCl_3$ molecule at 77 K,[1,3,4] as evidenced by a large anisotropic coupling [$A_{\parallel}$ (^{35}Cl) = 84.4 G[1]; G = 10^{-4} T] to a single chlorine nucleus. Here we report the e.s.r. characterization of a similar σ* complex between the radical cation of trimethyl phosphate and a $CFCl_3$ molecule, and show that the thermal and photolytic dissociation of this complex is accompanied by hydrogen atom transfer from a methyl group to the unique oxygen atom of the phosphate ester cation.

As shown in Figure 1(a), the e.s.r. spectrum of the trimethyl phosphate radical cation in $CFCl_3$ is composed of easily recognizable quartet features from hyperfine interactions with ^{35}Cl and ^{37}Cl nuclei, these features being split into doublets by an additional interaction with a nucleus of $I = \frac{1}{2}$. This doublet splitting can be assigned to the ^{31}P nucleus since an identical hyperfine pattern was obtained for the tri[^{2}H$_3$]methyl phosphate radical cation. The e.s.r. parameters for the two isotopic species fall in the following ranges: $A_{\parallel}$ (^{31}P)/G 25.6—26.7; $A_{\parallel}$ (^{35}Cl)/G 82.3—85.9; $A_{\parallel}$ (^{37}Cl)/G 68.4—71.3; $A_{\parallel}(^{35}$Cl)/$A_{\parallel}(^{37}$Cl) 1.200—1.208; $g_{\parallel}$ 2.0035—2.0046; temperature range 84—125 K; the chlorine hyperfine coupling is ca. 2.5% smaller for the deuteriated cation and shows a small negative temperature coefficient between 84 and 125 K.‡ Since the chlorine coupling (ca. 84 G) is remarkably close to the value of 84 G for the methyl formate cation,[1] a very similar type of solvent complex is indicated in the present case.

Above 115 K, the $(MeO)_3PO^+$–$CFCl_3$ complex undergoes a measurable thermal decay ($t_{\frac{1}{2}}$ ca. 10 min at 130 K) that is accompanied by a simultaneous growth in e.s.r. signals located between the inner components of the cation spectrum. For the protiated species, the e.s.r. spectrum of the decay product [Figure 1(b)] is a well defined triplet of doublets, the

triplet structure showing the typical anisotropy resulting from coupling to two α-hydrogen atoms [$A(2H)$ = 21.8 G] in a carbon-centred radical while the doublet splitting [$A(^{31}$P) = 10.5 G] also observed in the deuteriated radical is judged to be
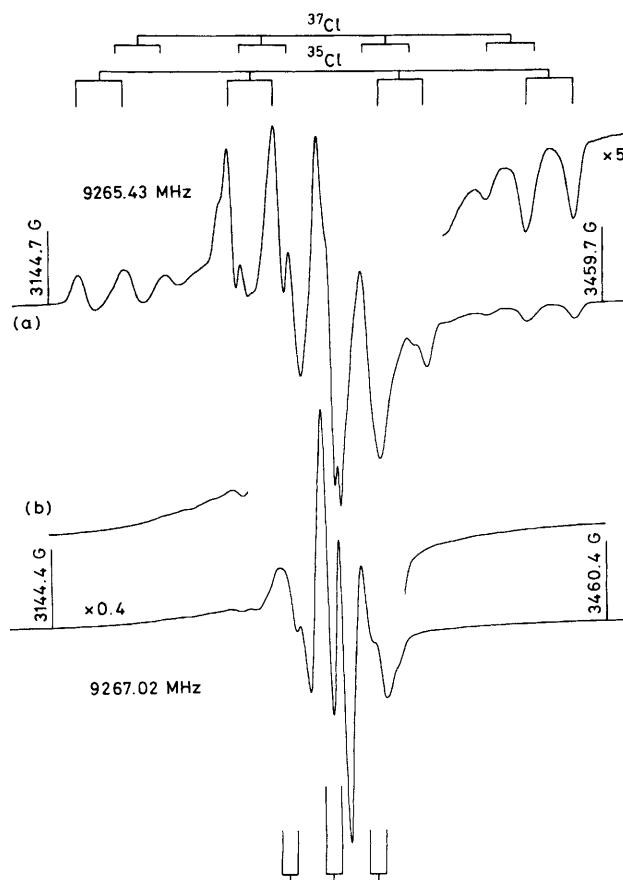
Figure 1. First-derivative e.s.r. spectra of a γ-irradiated $(MeO)_3PO$–$CFCl_3$ solid solution (dose, 0.3 Mrad) recorded at 105 K (a) before and (b) after annealing for 5 minutes at 135 K. The spectra were recorded under exactly the same conditions except where different gain factors are indicated.
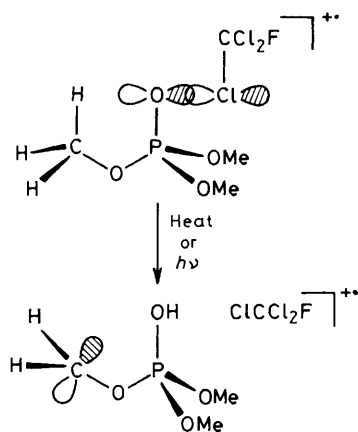
Figure 2. Structural representations of the $(MeO)_3PO–CFCl_3$ σ^* complex and of the carbon-centred radical produced by hydrogen atom transfer on dissociation.

isotropic from the sharp appearance of the two central components. These hyperfine parameters are similar to those reported for the $(MeO)_2P(O)OCH_2$ radical[5,6] and the spectrum is assigned to the $(MeO)_2P^+(OH)OCH_2$ radical formed by hydrogen atom transfer as depicted in Figure 2. Photolysis of the complex with visible light also brings about this transformation at temperatures below 115 K.

These results are of interest in two connections. First, the remarkable similarity between the $A_{||}$ (^{35}Cl) values for the methyl formate and trimethyl phosphate σ^* complexes is in accord with the expected dependence of the bonding on the difference between the ionization potentials (I.P.s) of the $CFCl_3$ solvent and the solute.[1,3] Since the I.P.s of methyl formate[7] and trimethyl phosphate[8] are both exactly equal to 10.81 eV, the results strongly support the argument that $\Delta I.P.$ is an important factor.[1,3] It should be stressed, however, that other considerations may also be significant,[1,3] and it is pertinent to point out that despite the very different overall chemical structure of these two molecules, the SOMOs of the two cations are in fact very similar, the unpaired electron being largely localized in a $2p_\sigma$ orbital on oxygen in each case.

The second interesting result of this work is that the thermal hydrogen atom transfer reaction provides direct confirmation of a 'McLafferty rearrangement'[9,10]§ suggested more than 20

§ McLafferty rearrangements have also been observed by e.s.r. spectroscopy in the cation radicals of carboxylic esters (see refs. 1 and 4).

years ago[11] to explain the formation of dialkyl acid phosphates as radiolysis products of trialkyl phosphates, a serious problem encountered in the reprocessing of nuclear fuels. Since it is now known that trialkyl phosphates undergo dissociative electron capture with the elimination of an alkyl radical,[6,12] simple proton transfer from the rearranged cation (Figure 2) to the $(RO)_2P(O)O^-$ anion would provide a simple mechanism for acid phosphate production.

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