

## Photochemical Dehalogenation of Carbon Tetrachloride by Alcohols Catalysed by Polyoxotungstates

Daryush Sattari and Craig L. Hill\*

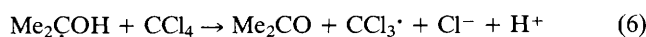
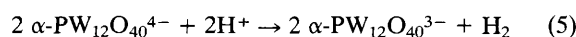
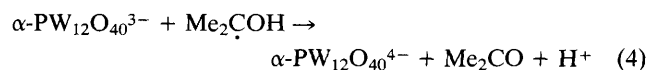
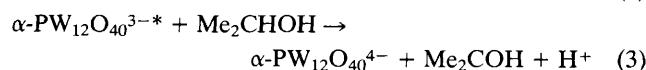
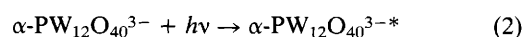
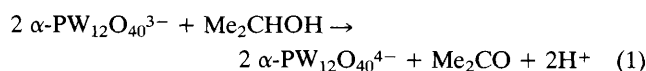
Department of Chemistry, Emory University, Atlanta, Georgia 30322, USA

Some polyoxotungstates, and in particular  $W_{10}O_{32}^{4-}$ , catalyse the reductive dehalogenation of carbon tetrachloride by alcohols upon irradiation under either aerobic or anaerobic conditions.

The generation of halogenated hydrocarbons and other halogenated compounds including pesticides, chemical weapons (*e.g.*, mustard gas), polychlorinated biphenyls (PCBs), and halogenated waste solvents constitutes a problem of some magnitude. Many of these compounds are carcinogenic and/or toxic and their release into the environment is a growing problem.<sup>1,2</sup> A number of new approaches to the dehalogenation of halocarbons has been reported recently. Some of note include dehalogenation by superoxide,<sup>2</sup> by the excited state of  $Rh^I$  complexes,<sup>3</sup> and by radicals derived from photolysis of alcohol-ligated Fe porphyrins.<sup>4</sup> We report here the photochemical dehalogenation of carbon tetrachloride using polyoxotungstate complexes. The application of polyoxometallates to this and other environmental problems has attracted us for several reasons: these compounds are robust; they can function as catalysts for potent thermal and photochemical oxidation processes; many are accessible in quantity; and considerable pharmacological and medical data now available, indicate that they are themselves very low in toxicity.<sup>5,6</sup>

The catalytic photochemical oxidation of alcohols by some polyoxometallates using  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$  for purposes of illustrations, equation (1), has been studied by several groups and equations (2)–(4) are generally proposed as the mechanism for these processes.<sup>7</sup> Reoxidation of the reduced complex either by  $H_2$  evolution, equation (5), or by  $O_2$  added to the system renders the overall process catalytic in polyoxometallate. The high yields of alcohols and autoxidation products generated when saturated hydrocarbons are photooxidized by  $W_{10}O_{32}^{4-}$  in the presence of  $O_2$  experimentally implicate high yields of freely diffusing radical intermediates.<sup>8</sup> Given these points and the high quantum yields for substrate oxidation, equation (1) (typically 0.1 or higher for alcohols<sup>7</sup> and considerably higher for alkanes in some systems<sup>9</sup>), and the fact that dehalogenation of halocarbons by radicals, equation (6), is a well known and facile process,<sup>4,10</sup> we felt that the intermediate radicals generated in this catalytic manner could

be directly used to dehalogenate halocarbons with some efficiency. This proved to be the case.



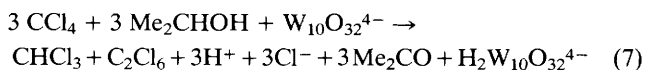
Solutions of a representative halocarbon,  $\text{CCl}_4$ , and one of two polyoxotungstates, the heteropoly compound,  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ , and the isopolytungstate,  $W_{10}O_{32}^{4-}$ , in one of four solvents were irradiated (550-W Hg lamp;  $\lambda > 280$  nm cut-off). Three of the solvents are readily photo-oxidized by both of these polyoxotungstates in the absence of halocarbons [a primary alcohol, EtOH, a secondary alcohol, propan-2-ol, and *N,N*-dimethylformamide (DMF)], and one is not (acetonitrile).<sup>7</sup> The degree of  $\text{CCl}_4$  dehalogenation observed was proportional to the degree of light absorption by the polyoxotungstate over the wavelength range of the incident light and the photoredox quantum yields of each complex in each solvent in the absence of  $\text{CCl}_4$  (Table 1). One reaction was examined in detail, the photochemical dehalogenation of  $\text{CCl}_4$  by  $W_{10}O_{32}^{4-}$  in propan-2-ol. The products from this reaction are chloroform, hexachloroethane, chloride ion, acetone, protons, and the protonated two-electron reduced form of the complex, equation (7). Although the quantities of all of the

**Table 1.** Anaerobic photodehalogenation of carbon tetrachloride by alcohols and DMF catalysed by polyoxotungstates in different solvents.<sup>a</sup>

Reaction no.	P <sup>b</sup>	Substrate	Solvent	Mol ratio <sup>c</sup>	% Conversion <sup>d</sup>	hν/h
1	α-H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	CCl <sub>4</sub>	EtOH	21.0	30.0	8.0
2	Na <sub>4</sub> W <sub>10</sub> O <sub>32</sub>	CCl <sub>4</sub>	PrOH <sup>e</sup>	10.0	78.0	5.0
3	Q <sub>4</sub> W <sub>10</sub> O <sub>32</sub> <sup>f</sup>	CCl <sub>4</sub>	MeCN	15.0	6.2	21
4	Na <sub>4</sub> W <sub>10</sub> O <sub>32</sub>	CCl <sub>4</sub>	MeCN <sup>g</sup>	11.5	36.0	7.0
5	Na <sub>4</sub> W <sub>10</sub> O <sub>32</sub>	CCl <sub>4</sub> <sup>h</sup>	DMF	87.0	93.5	7.0
6	Na <sub>4</sub> W <sub>10</sub> O <sub>32</sub>	CCl <sub>4</sub>	EtOH <sup>e</sup>	67.0	66.0	8.0
7	Q <sub>4</sub> W <sub>10</sub> O <sub>32</sub> <sup>f</sup>	CCl <sub>4</sub>	EtOH <sup>e</sup>	59.0	61.0	8.0
8	Q <sub>4</sub> W <sub>10</sub> O <sub>32</sub> <sup>i</sup>	CCl <sub>4</sub>	MeCN	60.0	63.0	8.0
9	Q <sub>4</sub> W <sub>10</sub> O <sub>32</sub> <sup>i</sup>	CCl <sub>4</sub>	DMF	40.0	~100	8.0

<sup>a</sup> Samples irradiated in 25-ml Schlenk flasks under 100% argon using 550-W medium-pressure Hg arc lamp at 22 °C. <sup>b</sup> P = polyoxotungstate; [P] ~2 × 10<sup>-3</sup> M in all reactions. <sup>c</sup> Moles substrate/moles of initial polyoxotungstate. <sup>d</sup> [1-(moles CCl<sub>4</sub> at end of reaction/moles CCl<sub>4</sub> initially)]/[100]. <sup>e</sup> Catalyst partially soluble. <sup>f</sup> Q = tetra-n-butylammonium ion. <sup>g</sup> Contained 1.35 × 10<sup>-1</sup> M butan-2-ol. <sup>h</sup> Contained 1.78 × 10<sup>-1</sup> M propan-2-ol. <sup>i</sup> Same conditions as other reactions except run under air ('zero grade').

products may approach the indicated stoichiometry at early reaction times, it is difficult to establish the relative quantities of these products as three of them, chloroform, hexachloroethane, and chloride are susceptible to further oxidation under the reaction conditions. The reoxidation of H<sub>2</sub>W<sub>10</sub>O<sub>32</sub><sup>4-</sup> to W<sub>10</sub>O<sub>32</sub><sup>4-</sup> by evolution of H<sub>2</sub>, was sufficiently fast that several turnovers could be achieved under these anaerobic conditions (see Table 1).



The kinetics for equation (7) at low substrate conversion proved to be first order in W<sub>10</sub>O<sub>32</sub><sup>4-</sup> in the optically dilute concentration regime and first order in light intensity. The order with respect to CCl<sub>4</sub> and propan-2-ol, however, varied between zero and one depending on the exact conditions. The mechanism of equation (7) is clearly complex. Table 1, reaction 3 (*i.e.*, no readily photo-oxidized solvent present) establishes that there is at least one path for dechlorination that does not involve solvent derived species. The major dechlorination process in the overall reactions is probably equation (6) which is rate determining.

The addition of O<sub>2</sub> to the reactions not surprisingly results in more rapid and more efficient removal of CCl<sub>4</sub> (*i.e.*, reactions 8 and 9, Table 1). The reduced polyoxotungstates are known to be reoxidized fairly rapidly by O<sub>2</sub><sup>5,7</sup> and the most likely initial kinetic reduction product in these reactions, superoxide, is known to dehalogenate a range of halocarbons in some solvents.<sup>2</sup> These aerobic reactions are clearly very complex and the rate behaviour confirms this. Several radical chain processes with different chain carrying intermediates are possible.<sup>10</sup> The scope and mechanisms of both the anaerobic and aerobic catalytic halocarbon dehalogenation reactions are under current investigation.

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