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Catalytic Carbon–Halogen Bond Cleavage Chemistry by Redox-Active Polyoxometalates

Daryush Sattari and Craig L. Hill*

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322

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Abstract: The use of redox-active polyoxotungstate complexes to effect the cleavage of carbon–halogen bonds (C–X, X = Cl or Br) by three distinct modes is demonstrated for the first time. The first mode involves direct thermal reaction of halocarbon substrates with $H_2W_{10}O_{32}^{4-}$ or α-$HPW_{12}O_{40}^{3-}$. The rate law for CCl_4 dehalogenation is $V = k(H_2W_{10}O_{32}^{4-})(CCl_4)$ and $k(H_2W_{10}O_{32}^{4-})/k(\alpha\text{-}HPW_{12}O_{40}^{3-}) = 2.8$. Several lines of evidence collectively establish that carbon–halogen bond cleavage likely involves dissociation electron transfer for the mode 1 reactions, although halogen atom abstraction (atom transfer) cannot be ruled out. The evidence includes comparisons of kinetic profiles for dehalogenation rate versus halocarbon substrate structure, relative reactivities of substrates (polyhalogenated more reactive (>) than monohalogenated compounds; tertiary > secondary > primary halides; bromides > chlorides), and other product distribution data including one "radical clock" reaction, in addition to the rate law. Interestingly one carbocation derived product, *N-tert*-butylacetamide, is generated in the debromination of *tert*-butyl bromide in acetonitrile. The second and third modes of dehalogenation involve extensions of previously reported polyoxometalate photoredox processes, and both modes are catalytic extensions of existing effective stoichiometric dehalogenation processes. The second mode proceeds by a complex rate law and involves photocatalytic transformation of organic halide (halocarbons) into inorganic halide (HX) coupled with the oxidation of sacrificial organic reductants (secondary alcohols or tertiary amides). The second mode essentially defines a method to catalytically generate reducing radicals under mild conditions; the radicals are the principal dehalogenating species. The third mode of dehalogenation is similar to the second mode but run in the presence of O_2. Here the reduced polyoxotungstates reduce O_2 to superoxide which then dehalogenates substrate. The third mode effects catalytic dehalogenation of a wide range of halocarbons.

Introduction

The extensive and alterable redox, structural, and other physical characteristics of some early transition metal–oxygen anion clusters, more succinctly called polyoxometalates or polyoxoanions, make this large class of inorganic complexes of interest in many areas of research.[1] Recent research has addressed the systematic coupling of thermal redox, photoredox, and other chemical reactions of polyoxometalates for the oxidative dehydrogenation, acylation, and coupling of hydrocarbons,[2-8] combining of oxidative and reductive processes in one-pot catalytic reactions,[9] modulation of organic radical reactivities,[5-7] and formulation of new processes for microlithography.[10] We report here the systematic coupling of thermal redox, photoredox, and other chemical reactions of polyoxometalates to effect the catalytic cleavage of carbon–halogen bonds. The structures of the two principal polyoxometalates used in this study, the Keggin heteropolytungstate, α-$PW_{12}O_{40}^{3-}$, and the isopolytungstate, $W_{10}O_{32}^{4-}$, are depicted in Figure 1.

Carbon–halogen bond cleavage is an issue of fundamental as well as practical interest. Carbon–halogen bond cleavage has played a major role in elucidation of the mechanism of organometallic transformations, particularly oxidative addition to transition metal centers,[11] it is of central importance in the formation of Grignard reagents, a mainstay in organic synthesis for seven decades,[12] and it has been a vehicle for defining the application of some rate-driving force relationships to dissociative

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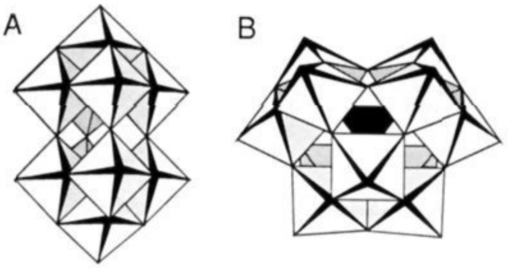

Figure 1. The structure of the isopolyanion decatungstate, $W_{10}O_{32}^{4-}$ (A), and the Keggin heteropolyanion, α-$X^{n+}W_{12}O_{40}^{(8-n)-}$ (B), in polyhedral notation. In polyhedral notation the vertices of the polyhedra represent the nuclei of the oxygen atoms while the metal ions are internal to the polyhedra and not directly seen. The heteroatom in B, X^{n+}, lies in the central T_d cavity of the molecule and is shaded more darkly than the other coordination polyhedra (all MO_6 octahedra in these two particular classes of polyoxometalates).

electron transfer processes at electrode interfaces.[13] The practical interest in processes that cleave carbon–halogen bonds, particularly carbon–chlorine and carbon–bromine bonds derives from the generic toxicity and carcinogenicity of this ubiquitous class of organic materials.[14] Major classes of erstwhile pesticides that persist in the environment and the most common chemical warfare agent, mustard (HD),[15] are chlorocarbons while the deleteriousness of chlorofluorocarbons with respect to the ozone layer derive largely from their chlorine content. Halogenated solvents continue to be produced and utilized, however, as they still remain the best solvents for some high technology processing (chip manufacture), a number of reactions in homogeneous catalysis, and dissolution of fluoropolymers and chlorofluorocarbon polymers. The quest for environmentally friendly catalysis and technology, in general, has given rise to a substantial thrust to get away from chlorocarbons and halogenated materials altogether.

The thermal debromination of polyhaloalkanes by reduced cobalt dodecatungstates[16] and the photochemical dechlorination of CCl_4 by polyoxotungstates[17] have been reported. We report here a thorough study of dehalogenation by polyoxometalates. The scope of this reaction is broad, and three distinct modes of carbon–halogen bond cleavage are demonstrated for the first time. The first involves direct thermal reaction of reduced polyoxotungstates with aliphatic halides. The second involves catalytic photochemical generation of reducing organic radicals which then dehalogenate the halocarbon substrate. This second mode is a catalytic extension of the well-investigated stoichiometric cleavage of carbon–halogen bonds by carbon-based radicals.[18] The third mode involves catalytic generation of superoxide which subsequently dehalogenates the substrate. This mode is also a catalytic extension of an effective stoichiometric process, the superoxide-based dehalogenation chemistry of Sawyer and co-workers.[19] Appropriate application of the extensive thermal and photochemical redox characteristics of some polyoxometalates facilitates the catalytic chemistries reported here.

Experimental Section

Materials and General Methods. The oxidized polyoxotungstates, $Q_4W_{10}O_{32}$,[20] **1**, $Na_4W_{10}O_{32}\cdot nH_2O$,[5] α-$H_3PW_{12}O_{40}\cdot nH_2O$,[21a] and α-$Q_3PW_{12}O_{40}$,[21b] and the complex $QClO_3$[22] (Q = tetra-*n*-butylammonium cation) were prepared and purified by literature methods. All the organic substrates, $QClO_4$, and aqueous NaClO were commercial samples and were used as received. Electronic absorption spectra were measured using a Hewlett-Packard 8451A multidiode array instrument, and the infrared spectra were obtained as KBr pellets (2–4 wt % of sample) on either a Nicolet 510M FTIR or a Perkin-Elmer Model 1430 instrument. ^{1}H and ^{31}P NMR spectra were obtained using GE QE-300 or WP200SY spectrometers, respectively. Quantitative analysis of the organic products was conducted using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a 25-m × 0.2-mm 5% phenyl methyl silicone capillary column, nitrogen as the carrier gas, and a Hewlett-Packard 3390A integrator. Gas chromatographic/mass spectral (GC/MS) analyses using a Hewlett Packard 5890 Series II GC coupled with a Hewlett Packard 5971A mass selective detector were also conducted to confirm product assignments. A few GC/MS analyses were conducted by EcoTek Laboratories Serivces of Atlanta, GA.

A general consideration in kinetics, product distribution, or other studies involving analysis of alkyl halides by gas chromatography (or GC/MS) is that many of these substrates are susceptible to thermal degradation, usually dehydrohalogenation, in the hot injector port of the chromatograph. These circumstances are exacerbated by the fact that there is no facile chemical or physical method to quench the reaction by dehalogenating unreated halocarbon prior to analysis without altering the other species in solution. A series of control reactions indicated that all the halocarbon substrates examined in this work except *tert*-butyl bromide were stable under the conditions of analysis. For reactions with *tert*-butyl bromide, substantial dehydrohalogenation was usually seen but the degree of degradation appeared to be relatively unaffected by the presence of polyoxometalate. Reactions involving *tert*-butyl bromide were corrected for thermal decomposition.

Kinetics of Direct Thermal Stoichiometric (Mode 1) Dehalogenation. These experiments involved the reaction of authentic reduced polyoxotungstates with halocarbons under an inert atmosphere. The authentic reduced polyoxotungstate reactants could be generated, in principle, by chemical, electrochemical, or photochemical methods. The latter were chosen for convenience and for being minimally obtrusive to the subsequent dehalogenation reactions (large quantities of supporting electrolyte mandated by controlled potential electrolysis were to be avoided in the kinetics studies). The reduced complexes were generated by photochemical reduction in the presence of 2-butanol, as exemplified in eq 1 for decatungstate. These photoredox reactions have been known for over

$$W_{10}O_{32}^{4-} + h\nu + C_2H_5CHOHCH_3 \rightarrow W_{10}O_{32}^{6-} + C_2H_5COCH_3 + 2H^+ \quad (1)$$

10 years and have been demonstrated to proceed cleanly and in high yield by several groups.[8] The reduced polyoxotungstates used in this paper were stable in the absence of the alkyl halides for times longer than those used in the experiments in this paper.[3b,5,6]

In order to obtain interpretable results the oxidation states and protonation states of the reduced polyoxotungstate reactants and the reactivity of the products under the reaction conditions had to be evaluated.

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Oxidative titration of photoreduced α-$PW_{12}O_{40}^{3-}$ and $W_{10}O_{32}^{4-}$ complexes by Ce^{IV}, using the previously reported procedure,[3b] was straightforward and led to 1.0 ± 0.05 and 1.6 ± 0.05 electrons per polyoxotungstate, respectively. As described previously,[6] the photochemical production of reduced decatungstate in aprotic organic media in the absence of external sources of protons leads to a mixture of one- and two-electron reduced forms of the complex $W_{10}O_{32}^{5-}$ and $W_{10}O_{32}^{6-}$, respectively, whose concentrations can be simultaneously quantified by an algebraic and graphic method using the previously documented absorption spectral characteristics: for $W_{10}O_{32}^{5-}$, λ_{max} = 780 nm and $\epsilon_{780,1e} \sim 7500$ M^{-1} cm^{-1};[20,23] and for $W_{10}O_{32}^{6-}$, λ_{max} = 622 nm and $\epsilon_{622,2e}$ = 15 500 M^{-1} cm^{-1}.[5,8j,20] The concentrations contained in this manner correlate with cyclic voltammetric results. In addition to this analysis, a set of kinetic control curves (λ_{max} values at 780, 622, and 330 nm as a function of time) were consistent with the features at 780 and 622 nm being principally derived from $W_{10}O_{32}^{5-}$, $W_{10}O_{32}^{6-}$, and the oxidized form, $W_{10}O_{32}^{4-}$, respectively. The kinetics of $W_{10}O_{32}^{6-}$ disappearance and $W_{10}O_{32}^{4-}$ appearance were taken as proportional to the time dependence of the 622- and 330-nm features, respectively.

Although potentiometric titration of standard oxidized polyoxometalates in organic media to determine protonation state has been documented to be an effective procedure,[24] potentiometric titration of reduced polyoxometalates was not prior to this study. The titrations of both reduced polyoxotungstates, α-$PW_{12}O_{40}^{4-}$ and $W_{10}O_{32}^{6-}$ were successfully carried out by adding degassed 1.0 M methanolic (n-Bu_4N)OH to magnetically stirred 15-mL portions of 6.0 mM anaerobic acetonitrile solutions of the photoreduced complexes. Both reduced polyoxotungstates gave reproducible curves (Figure S1 in supplementary material). Although the end points are less distinct for $W_{10}O_{32}^{6-}$ than α-$PW_{12}O_{40}^{4-}$ as a result of the presence of some $W_{10}O_{32}^{5-}$, the presence of two protons per $W_{10}O_{32}^{6-}$ is clearly inferred. The oxidative and potentiometric titrations coupled with the spectroscopic data establish that the reacting species for the reduced decatungstate and dodecatungstophosphate systems are $H_2W_{10}O_{32}^{4-}$ and α-$HPW_{12}O_{40}^{3-}$, respectively.

In a typical reaction, 0.66 mmol of 2-butanol sacrificial reductant was added to 4.0 mL of degassed dry acetonitrile containing 0.132 mmol of $Q_4W_{10}O_{32}$ and internal standard under argon in a 2-mm-pathlength quartz cuvette at 25 ± 0.5 °C. This solution was irradiated at this temperature until all the $W_{10}O_{32}^{4-}$ had been reduced. The reduction reaction generating $H_2W_{10}O_{32}^{4-}$ and the subsequent dehalogenation process regenerating the oxidized complex, $W_{10}O_{32}^{4-}$, were both monitored by the intensity of the chromophore at 330 nm, the absorption maxima of $Q_4W_{10}O_{32}$. The carbon tetrachloride solution was degassed and kept under argon throughout all experiments. To determine the order with respect to carbon tetrachloride, varying amounts of this substrate, (see Figure 2, top, in the Results and Discussion section) were added by syringe to the reduced polyoxotungstate. To determine the order with respect to $H_2W_{10}O_{32}^{4-}$, 0.1 mL of carbon tetrachloride (final concentration 0.2 M) was added to a series of solutions of $H_2W_{10}O_{32}^{4-}$ in acetonitrile varying from 0.8 to 4.0 mM (4.0-mL volume in each case) under argon at 25 °C. All these reactions were run in duplicate.

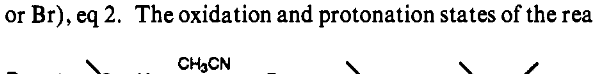
Direct Thermal Stoichiometric (Mode 1) Product Distribution Studies. In order to have the most useful product studies, the reactions in this mode were run using appropriate stoichiometric amounts of the reduced polyoxotungstate and halocarbon substrates. In a typical reaction, 0.132 mmol of degassed CCl_4 was added via syringe to 0.132 mmol of reduced decatungstate in ca. 4 mL of acetonitrile generated as described above in the mode 1 kinetics studies. The identical procedure was followed for reactions involving reduced dodecatungstophosphate but 0.04 mmol each of CCl_4 and α-$HPW_{12}O_{40}^{3-}$ rather than 0.132 mmol were used as a consequence of solubility limitations. The reactions were conducted at 60 ± 0.1 °C (thermostated bath) in quartz cuvettes fitted with Teflon stopcocks and standard-taper side arms. The final products were identified and quantified as described above (Materials and General Methods). For the dechlorination of neophyl chloride, 0.0374 g (0.222 mmol) of neophyl chloride was added to 3.0 mL of a 3 mM solution of $H_2W_{10}O_{32}^{4-}$ (0.009 mmol) prepared photochemically as described above in a 2-mm-pathlength quartz cuvette under argon. The reaction was maintained at 25 ± 0.5 °C. The only detectable product, *tert*-butylbenzene, was determined by coinjection with an authentic sample and by GC/MS analysis and was quantified by GC as described above. For the carbocation trapping experiment in conjunction with dehalogenation of *tert*-butyl bromide, the regular reaction and analysis procedure was followed except that 4 equiv of water per equiv of $H_2W_{10}O_{32}^{4-}$ were added after irradiation and prior to addition of *tert*-butyl bromide substrate.

Catalytic Photochemical Anaerobic (Mode 2) (Table II) and Aerobic (Mode 3) (Table III) Dehalogenation. In a typical anaerobic reaction (mode 2), 0.033 g (0.01 mmol) of $Q_4W_{10}O_{32}$, 0.150 g (0.97 mmol) of carbon tetrachloride, the organic halide substrate, and 0.1 mmol of a sacrificial reductant (usually 2-butanol or 2-propanol) were dissolved in 5 mL of acetonitrile contained in a Pyrex Schlenk flask equipped with Teflon stoppers. The contents of the reactions were degassed, placed under argon, and then irradiated using a 1000-W high-pressure Hg lamp through Pyrex (λ > 280 nm). All reactions were carried out at 25 ± 0.5 °C and the contents were magnetically stirred in all cases. Similar reaction conditions were used for the control reactions involving the attempted organic halide oxidation by hypochlorite, chlorate, or perchlorate salts except that the concentration of these salts was 0.3 M and no alcohol sacrificial reductant was present. The aerobic reactions (mode 3) were prepared and conducted in a manner similar to the anaerobic reactions except that the argon atmosphere was replaced with 100% O_2 (zero grade) prior to irradiation (mol ratio of O_2 to $W_{10}O_{32}^{4-} \sim 100$) and the additional secondary alcohol sacrificial reductant was often absent. In these cases, the solvent served as the sacrificial reductant with *N,N*-dimethylformamide being far more effective than acetonitrile.

Kinetic Measurements of Catalytic Anaerobic (Mode 2) Dehalogenation. The same apparatus and temperature (25 ± 0.5 °C) were used for these kinetics studies as the ones described above for mode 1 (thermal) dehalogenation. The most convenient way to monitor the reactions involved the appearance of the 622-nm absorption maximum characteristic of $H_2W_{10}O_{32}^{6-}$. The reactions were run under pseudo-first-order and optically dense conditions, where appropriate, and initial rate methods were used. The light intensity and the concentrations of $W_{10}O_{32}^{4-}$, CCl_4, and 2-propanol were varied over the ranges given in Figures S2, S3, S4, and S5 (supplementary material) with the invariant concentrations as follows: [$W_{10}O_{32}^{4-}$] = 4 mM; [CCl_4] = 160 mM; [2-C_3H_7OH] = 110 mM. Reactions were irradiated with a 1000-W ozone-free Xe arc lamp (Oriel) equipped with 10-cm water bath infrared and Pyrex (λ > 280 nm) cutoff filters. The rate dependence on light intensity was determined using neutral density filters to decrease irradiance intensity. In several reactions, there was a detectable background reaction involving production of reduced decatungstate by photooxidation of the acetonitrile solvent. The rate measurements were corrected for this reaction.

Results and Discussion

Dehalogenation Mode 1: Stoichiometric Direct Thermal Dehalogenation of Aliphatic Halocarbons by Reduced Polyoxoanions. The representative reduced isopolytungstate, $H_2W_{10}O_{32}^{4-}$, and heteropolytungstate, α-$HPW_{12}O_{40}^{3-}$, both reduce aliphatic halocarbons. The organic product distributions, summarized in Table I for reaction with representative tertiary, secondary, primary, and polyhalogenated substrates, are dominated by dehalogenation products (alkanes and alkenes in the case of the monohalo substrates), dimers, and inorganic halide, X^- (X = Cl or Br), eq 2. The oxidation and protonation states of the reactive reduced forms of the polyoxotungstates were established by oxidative and potentiometric titration, respectively, to be the doubly protonated two-electron reduced form of decatungstate, $H_2W_{10}O_{32}^{4-}$, and the singly protonated one-electron reduced form of Keggin heteropolytungstate, α-$HPW_{12}O_{40}^{3-}$ (see Experimental Section). The five halocarbons examined in the product studies (carbon tetrachloride, bromotrichloromethane, 1-bromodecane, bromocyclohexane, and 2-bromo-2-methylpropane (*tert*-butyl bromide)) and the seven additional ones examined in the kinetics studies (1-pentyl, neopentyl, benzyl, cyclobutyl, cyclopentyl, cycloheptyl, and phenyl bromides) were specifically chosen as those compounds have diverse, distinct, and well-documented



alkene + X^- + trace other organic products (2)

$P_{red} = H_2W_{10}O_{32}^{4-}$ or $HPW_{12}O_{40}^{3-}$

P_{ox} = oxidized deprotonated form of complex

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Table I. Product Distributions in Thermal Reductive Dehalogenation of Representative Halocarbons by Reduced Polyoxotungstates[a]

P_{red}[b]	RX	conversion (%)[c]	products (yield %)[d]
$H_2W_{10}O_{32}^{4-}$	CCl_4	26.0	$CHCl_3$ (82); C_2Cl_6 (2.0)
$H_2W_{10}O_{32}^{4-}$	$CBrCl_3$	66.0	$CHCl_3$ (77); C_2Cl_6 (1.9)
$H_2W_{10}O_{32}^{4-}$	1-$C_{10}H_{21}Br$[e]	6.0	$C_{10}H_{22}$ (18); 1-$C_{10}H_{20}$ (13); $C_{20}H_{42}$ (5.0)
$H_2W_{10}O_{32}^{4-}$		8.0	 (39);  (42);  (8.0)
$H_2W_{10}O_{32}^{4-}$	t-C_4H_9Br	40.0	C_4H_{10} (18); C_4H_8;[f] C_8H_{18};[g] t-$C_4N_9NHC(O)CH_3$ (43)
$HPW_{12}O_{40}^{3-}$ [h]	CCl_4	14.0	$CHCl_3$ (5.0); C_2Cl_6[g]

[a] All reactions run under argon at 60 ± 0.1 °C for 24 h, $[RX]_0/[P_{red}]_0 = 1$; additional reaction conditions given in the Experimental Section. [b] P_{red} = photoreduced polyoxotungstate; $[H_2W_{10}O_{32}^{4-}] = 33$ mM; $[HPW_{12}O_{40}^{3-}] = 10$ mM. [c] $(1 - [RX]_t/[RX]_0) \times 100$, where $[RX]_t$ = quantity of RX at elapsed time of reaction (24 h). [d] Yield based on halocarbon substrate consumed. [e] Reaction run at 80 ± 0.1 °C. [f] There is considerable error in the yield of isobutene as the response factor was hard to evaluate and correction had to be made for significant competing thermal dehydrodehalogenation of unreacted *tert*-butyl bromide in the hot injector port of the chromatograph. [g] Below detectable limit (≪1%). [h] $[RX]_0/[P_{red}]_0 = 3$; reaction run at 75 ± 0.1 °C.

relative reactivities in halogen atom abstraction,[25] electron transfer reduction,[13] and nucleophilic displacement reactions (S_N2 or S_N1).[26] All these reactions, except for the control run in the presence of O_2, were conducted under anaerobic conditions to obviate not only autoxidation but also other radical processes that would make the interpretation of kinetics and product distribution data problematical. Although the relative rates of reaction of the halocarbon substrates and the products were assessed and this information indicated no potential problem from subsequent reactions of initial products, all kinetics involved initial rate methods and low conversions. Furthermore, the conversions in the product distribution studies (Table I) were kept low to minimize the effect of subsequent reactions. The cases where subsequent reactions were the most worrisome were the CCl_4 and $BrCCl_3$ reductions. Although one of the two detectable products in CCl_4 dechlorination reactions, hexachloroethane (C_2Cl_6), is slightly more reactive than CCl_4 itself, the relative concentrations of CCl_4 and C_2Cl_6 under the conditions in Table I resulted in negligible loss of the C_2Cl_6 product, thus the ratio of the products was reasonable and effectively constant.

Eight lines of evidence from the products and relative rates of these processes allow us to rule out several possible mechanisms discussed below. First, the rate law was determined for an exemplary reaction, that between $H_2W_{10}O_{32}^{4-}$ and CCl_4. Log–log plots from six reactions varying in $H_2W_{10}O_{32}^{4-}$ concentration and seven varying in CCl_4 concentration establish the process is first order in both reactants, eq 3 (Figure 2). Independently it

$$\text{rate} = k(H_2W_{10}O_{32}^{4-})(CCl_4) \qquad (3)$$

was established that for reduction of CCl_4, $k(H_2W_{10}O_{32}^{4-})/k(\alpha\text{-}HPW_{12}O_{40}^{3-}) = 2.8$. Second, for both reduced polytungstates, the polyhalogenated substrates are more reactive than the monohalogenated substrates. Third, the bromides are more reactive than the corresponding chlorides: $BrCCl_3$ is more reactive than CCl_4 and 1-bromodecane is more reactive than primary chlorides. Indeed primary chlorides are so unreactive with both reduced polyoxotungstates under the experimental conditions that none of the organic products from these reactions could be unequivocally established using either electron impact (in GC/MS analysis) or flame ionization detection.

The fourth and fifth lines of evidence derive from the types and relative quantities of the products in Table I. The products are typical of those derived from free organic radical intermediates: by far the dominant products are those derived from disproportionation and coupling. In order words the monohaloalkane substrates produce alkane, alkene, and dimer while the CCl_4 and $CBrCl_3$ substrates produce $CHCl_3$ and C_2Cl_6. The ratio of disproportionation to coupling products, for the low conversion kinetic product distributions in Table I, is equal to the ratio of bimolecular rate constants for the radical intermediates, k_d/k_c, eq 4. In most cases, however, the reduction products (alkane or

$$k_d/k_c = (\text{yield of alkene} \times 2)/(\text{yield of dimer}) \qquad (4)$$

$CHCl_3$) are more prevalent relative to the coupling products than can be accounted for solely by disproportionation and coupling of radicals.[27] This is consistent with two points: there are substantial concentrations of reduced polyoxotungstate present during these reactions and some reduced polyoxotungstates are known to reduce organic radical intermediates to carbanions in acetonitrile solution at these temperatures.[7] The addition of as little as 4 equiv of water per equiv of reduced polyoxotungstate in the debromination reactions results in an increase of the reduction products relative to the other products providing further

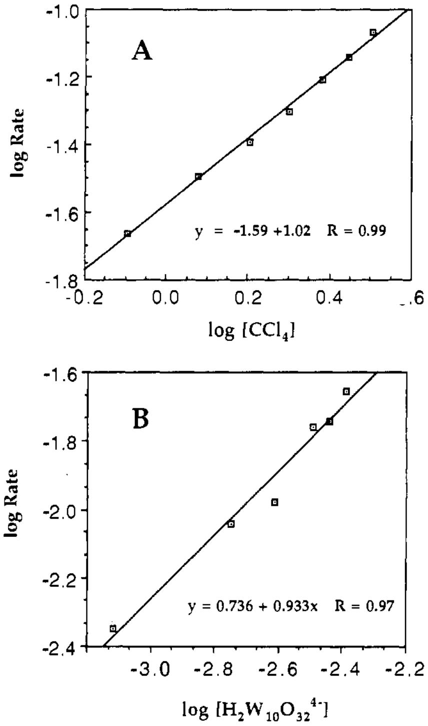

Figure 2. Log–log plots for the initial rates of reaction of $H_2W_{10}O_{32}^{4-}$ with CCl_4: (top) dependence on CCl_4 concentration; (bottom) dependence on $H_2W_{10}O_{32}^{4-}$ concentration. The equations in each box are the best fit lines through the experimental points with their correlation coefficients. All conditions are given in the Experimental Section.

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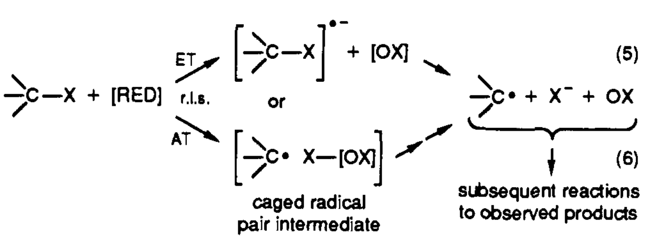
[25] Poutsma, M. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973, Chapters 14 and 15 and references cited therein.

[26] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; Chapter 4 and references cited therein.

[27] The ratio of alkene to dimer, resulting from disproportionation and coupling (combination) of alkyl radicals, respectively, although dependent on solvent (cf.: Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200), typically averages ~0.15, ~0.7, and ~2.8 for primary, secondary, and tertiary radicals, respectively, in nonviscous solvents at room temperature (cf.: Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441).

evidence for generation and subsequent reduction of intermediate organic radicals. An obvious additional line of potential evidence for radical intermediates in dehalogenation by reduced polyoxotungstates involves trapping of any intermediate alkyl radicals by radical scavengers. Not surprisingly, however, the usual radical scavenging experimental protocols did not provide significant information as in all cases tried, reaction with the scavengers was far faster than reaction with the alkyl halide substrates. Consequently no carbon-based radicals were effectively produced in the reactions containing scavengers.[28]

A sixth line of evidence was sought from comparisons of kinetic (substrate structure–reactivity) profiles for dehalogenation reactions that proceed by electron transfer (ET) and halogen atom abstraction (atom transfer or AT) with that for dehalogenation by $H_2W_{10}O_{32}^{4-}$. ET and AT mechanisms in context with reductive dehalogenation are depicted in minimal terms in eqs 5 and 6, respectively. Such kinetic profiles can delineate structural and electronic features of the transition state of the rate-limiting step (r.l.s., eqs 5 and 6) and are generally useful in ruling out several mechanisms. It should be noted that both mechanisms lead to carbon-based radicals and products in general qualifying the utility of some conventional radical trapping experiments. Arguments based on both theoretical and experimental data can be made that AT and ET represent extremes in a continuum of mechanism for reductive carbon–halogen bond cleavage. Significantly, however, it should be pointed out that AT and ET do apparently give rise to distinct kinetic product distributions in some cases such as oxidation of alkyl arenes[29] and alkanes.[30] We have chosen two reactions that represent the AT and ET limits in reductive dehalogenation: for the AT process, dehalogenation by tri-*n*-butyl tin radicals;[12b,31] for the ET process, dehalogenation by lithium 4,4-dimethylbenzophenone ketyl radical anion.[12c] Garst[32] and Whitesides[12c] have pointed out that a lack of S_N2 behavior on the part of ketyl radicals argues their reactivity with respect to alkyl halides is strongly ET in character. Comparison of the rate–structure profiles of dehalogenation by tri-*n*-butyl tin radicals and $H_2W_{10}O_{32}^{4-}$ is given in Figure 3A. Comparison of those for dehalogenation by 4,4-dimethylbenzophenone ketyl radical anion and $H_2W_{10}O_{32}^{4-}$ is given in Figure 3B. The correlation coefficient for the former plot ($R = 0.68$) is somewhat poorer than that for the latter ($R = 0.90$), but neither is exceptional. It should be noted, however, that the dehalogenation chemistry by $H_2W_{10}O_{32}^{4-}$ is in acetonitrile while that by the other two reagents is in ether solvents as the chemistry of $(n\text{-}Bu_4N)_4H_2W_{10}O_{32}$ is not compatible with ether solvents and the chemistry of the other two reagents is not optimally compatible with acetonitrile.



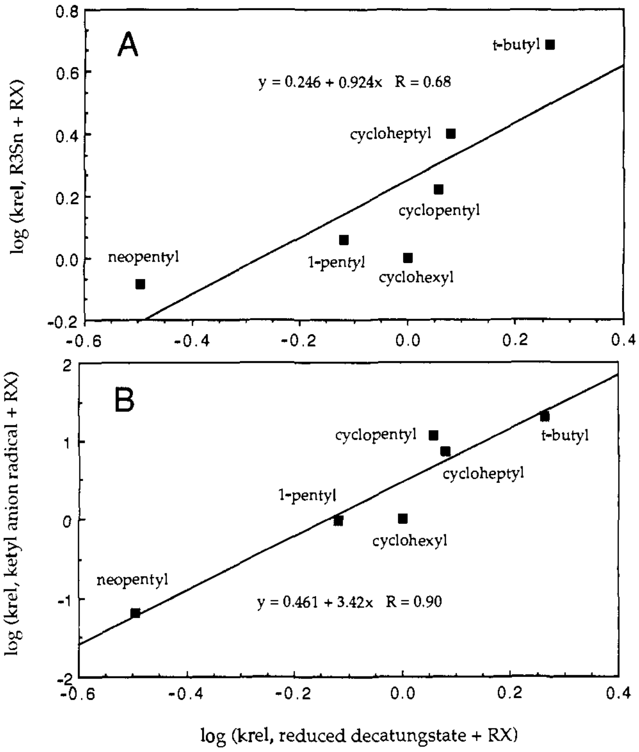


Figure 3. Rate–structure profiles of direct thermal reductive dehalogenation by $H_2W_{10}O_{32}^{4-}$ versus that by tri-*n*-butyl tin radicals, $n\text{-}Bu_3Sn^{\bullet}$ (diethyl ether at 0 °C),[12b,31] (**A**) and versus that by 4,4-dimethylbenzophenone ketyl radical anion, $(p\text{-}CH_3C_6H_4)_2COLi$ (tetrahydrofuran, 24 °C)[12c] (**B**). All rates are relative to that for cyclohexyl bromide. The equations in each box are the best fit lines through the experimental points with their correlation coefficients. The protocols and conditions for the polyoxotungstate rate measurements are given in the Experimental Section.

All the data cited to this point are consistent with some degree of alkyl radical intermediates in the reductive dehalogenation reactions, eq 2. More evidence as to the fate of such radicals would be very helpful. Two additional lines of evidence furnish data addressing the redox interception of intermediate radicals by the polyoxotungstate species. It is now well documented from pulse radiolysis studies[33] and from kinetic and products distribution analyses[6] that some high potential polyoxotungstates in their oxidized forms and ground electronic states, including $\alpha\text{-}PW_{12}O_{40}^{3-}$, oxidize organic radicals to carbocations at very high rates at room temperature in solution. At the same time, experimental evidence now strongly suggests that low potential polyoxotungstates in their reduced forms and ground electronic states, i.e. $W_{10}O_{32}^{6-}$, reduce organic radicals to carbanions under similar conditions.[7] The first experiment (the seventh line of evidence regarding mechanism) involved examination of the product distribution derived from dechlorination of 2-methyl-2-phenyl-1-chloropropane (common name: neophyl chloride). The corresponding radical, neophyl radical, rearranges with a known rate constant (59 s^{-1} at 25 °C) by a 1,2-phenyl shift to the benzyldimethylcarbinyl radical and as such constitutes a useful "radical clock".[34] At the same time, oxidation of this radical results in complete rearrangement to the benzyldimethylcarbinyl

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[28] For example, the reaction of bromocyclohexane, RBr, with $H_2W_{10}O_{32}^{4-}$ in the presence of O_2, one of the most effective radical scavengers known ($R^{\bullet} + O_2$ is nearly diffusion limited in most media, cf.: Benson, S. W.; Nangia, P. S. *Acc. Chem. Res.* **1979**, *12*, 223) did not produce the usual products derived from trapping alkyl radical intermediates with O_2, alkyl hydroperoxide (nor its dominant decomposition products, alcohol or ketone). Reduction of O_2 to water by the reduced polyoxotungstates was the only observed process.

[29] Oxidation of alkylarenes by strong one-electron transition metal oxidants can go by initial AT (most often involving hydrogen abstraction by oxy radicals derived from homolysis of the ligand–metal bonds of the initial complex) and by initial ET. Although ET and AT in such oxidations can lead to similar product distributions, in some cases the product distributions are distinct. Cf.: Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapter 5.

[30] Alkane oxidation by almost any radical species (AT) leads to products derived from the most substituted (often tertiary) radicals. In contrast, alkane oxidation by ET and subsequent deprotonation of the resulting alkane cation radical preferentially leads to products derived from the least substituted radicals: (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1981**, *103*, 3591. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Am. Chem. Soc.* **1987**, *109*, 4496.

[31] (a) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299. (b) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

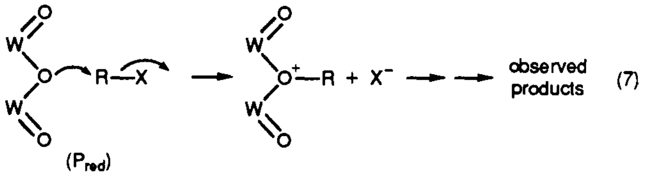
[32] Garst, J. F.; Smith, C. D. *J. Am. Chem. Soc.* **1979**, *98*, 1520.

[33] (a) Papaconstantinou, E. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 2769. (b) Lerat, O.; Chauveau, F.; Hickel, B. *New J. Chem.* **1990**, *14*, 37.

[34] (a) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224, 4692. (b) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

carbocation and then to the well-documented products derived therefrom (primarily the thermodynamically most stable alkene). Reduction of neophyl chloride by $H_2W_{10}O_{32}^{4-}$ leads only to *tert*-butylbenzene (2% yield and conversion); no isobutylbenzene derived from reduction of the benzyldimethylcarbinyl moiety was observed within the detectability limit of the analysis (<0.1%). This rules out the presence of long-lived alkyl radicals and carbocation intermediates in the dehalogenation of primary chlorides. In contrast, the eighth line of evidence follows from data in Table I—the dehalogenation of the tertiary halide, *tert*-butyl bromide, generates *N*-*tert*-butylacetamide in significant yield. This process is analogous to the Ritter reaction and almost certainly involves interception of intermediate *tert*-butyl carbocations by the solvent acetonitrile followed by hydrolysis. The formation of *N*-alkylacetamide products under formally reductive conditions is not outlandish. The oxidized form of the polyoxometalate is generated in the proximity of the organic unit after the initial reductive event, eq 2. Furthermore, hydrocarbon photooxidations in acetonitrile by polyoxotungstates when nearly all the polyoxotungstate is in the reduced form have been documented.[3a] The intermediacy of the tertiary carbocation, $[(CH_3)_3C]^+$, was corroborated by running the dehalogenation of *tert*-butyl bromide in the presence of as little as 4 equiv of water per equiv of reduced polyoxotungstate—*tert*-butyl alcohol was formed (~10% yield) and formed at the expense of the *N*-alkylacetamide product. Although no products derived from carbocation rearrangements (alkyl and hydride shifts) are seen in the dehalogenations, these products would not necessarily be expected under the reaction conditions. The collective evidence suggests that under the experimental conditions in Table I intermediate primary radicals are not significantly oxidized by polyoxometalates while intermediate tertiary radicals are.

Collective consideration of the eight lines of evidence above allows us to rule out several mechanisms for the reaction of organic halides with reduced polyoxotungstates. Although carbocations are well-known intermediates in the dehalogenation of tertiary halide substrates, an S_N1 process involving rate-determining formation of halide ion and carbocation is not likely to be operable in reactions with reduced polyoxotungstates. It is inconsistent with considerable evidence implicating the existence of radical intermediates and with the rate law, eq 3. A second mechanism for carbon–halogen bond cleavage involves direct nucleophilic attack by the oxygens of the reduced polyoxometalate at the halogen-bearing carbon atom. Such an attack would likely take place at the bridging oxygens as these have been shown theoretically and experimentally to be those with the highest negative charge densities and the most nucleophilic, eq 7.[1,35]



(7)

Furthermore an S_N2-like alkylation of an oxidized polyoxotungstate (unprotonated $\alpha\text{-}PW_{12}O_{40}^{3-}$) that is less nucleophilic than either of the reduced polyoxotungstates examined in this study, $H_2W_{10}O_{32}^{4-}$ and $\alpha\text{-}HPW_{12}O_{40}^{3-}$, by a strong alkylating agent (R_3O^+) is precedented.[35a] Although an S_N2-like process is compatible with the observed rate law and other data, it is quite unlikely based collectively on the observed reactivity order of the halocarbon substrate (tertiary > secondary > primary C–X), the facility of reaction of polyhaloalkane substrates and the products derived therefrom (C_2Cl_6 from CCl_4), the low but finite reactivity of a neopentyl type (neophyl) chloride, and the fact that even reduced polyoxometalates are poor nucleophiles even in polar aprotic media. Furthermore it is not likely that the alkoxy intermediate (alternative nomenclature: alkyl ester of the polyoxotungstic acid) could react further to cleanly give all the observed products. Equation 7 is even less likely for $P_{red} = \alpha\text{-}HPW_{12}O_{40}^{3-}$ than for $P_{red} = H_2W_{10}O_{32}^{4-}$ as the former can only function as a one-electron reductant and nucleophilic substitutions in either inorganic or organic systems are formally two-electron in nature. It should be noted, however, that transition metal centered S_N2-like processes that involve one electron are known, but they are rare and occur only in special cases.[36]

Two more mechanisms which are reasonable or precedented in other reactions of metal centers with alkyl halides, a mass transport limited process and oxidative addition to the metal center, can be ruled out for direct thermal dehalogenation of halocarbons by reduced polyoxotungstates. The best example of a mass transport limited reductive dehalogenation, and one with rigorous mechanistic documentation, is the Grignard reaction of alkyl bromides and iodides with Mg metal in ethers.[12] The rate law, slow absolute rates, and different rates of reaction with the two different types of reduced polyoxotungstates and several different types of halocarbon substrates firmly rule out diffusion limited processes for all the reduced polyoxotungstate dehalogenations. Conventional two-electron oxidative addition is highly unlikely not only as two open coordination positions are necessary on a single metal but also the presence of a two-electron-reduced tungsten atom is required. The observed reactivity profile (primary carbon centers least reactive) is also not optimally consistent with such an oxidative addition process.

The mechanisms not yet ruled out are halogen atom abstraction, an atom transfer process (AT), and electron transfer (ET). The experimental evidence and background information immediately following do not allow us to rule out either ET or AT as operable in the direct thermal dehalogenation of alkyl halides by reduced polyoxotungstates. Nevertheless both the experimental data (Figure 3) and literature studies of other reductive alkyl halide dehalogenations argue that ET is more likely than AT. Furthermore, the ET is likely dissociative in nature, that is, addition of the electron to the σ^* antibonding LUMO of the alkyl halide substrate is concerted with rupture of the carbon–halogen bond.

Although AT via formation of an initial oxygen–halogen bond is highly unfavorable kinetically (the exothermicity, which defines the minimum activation energy, is approximately +30 kcal/mol for dechlorination), abstraction by the reduced metal center (d^1, W^V), although probably still quite endothermic and slow, is possible in principle. Although polyoxometalates such as $H_2W_{10}O_{32}^{4-}$ and $\alpha\text{-}HPW_{12}O_{40}^{3-}$ are conventionally viewed as composed exclusively of coordinatively saturated metal centers, exchange of polyoxometalate oxygen with H_2O[37] or O_2[38] oxygen as well as heterogeneous catalytic oxidation studies[1e] implicate that metal centers can be reasonable intermediates in redox reactions in such polyoxometalates. One cannot unequivocally rule out intermediate cleavage of a tungsten–oxygen bond and halide abstraction by a resulting reduced (d^1) tungsten center in the polyoxometalate, eq 8, based on fundamental energetic and mechanistic information as well as polyoxometalate chemistry in the literature. There are a number of reasonable ways that the initial oxidized form of the polyoxotungstates, P_{ox} in eq 8, could be regenerated from the polyoxotungstate species participating in such a process, but since this regeneration is peripheral to our discussion here and data are not available to address this, we will

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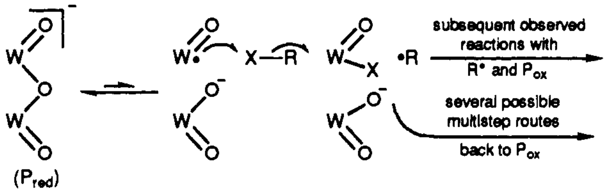
[35] For example see: (a) Knoth, W. J.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265. (b) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030. (c) Hahn, J. S.; So, H. *Bull. Korean Chem. Soc.* **1992**, *13*, 92 and references in footnote 1.

[36] For example, see: (a) Espenson, J. H.; Shveima, J. S. *J. Am. Chem. Soc.* **1973**, *95*, 4468. (b) Chrzastowski, J. Z.; Cooksey, C. J.; Johnson, M. D.; Lockman, B. L.; Steggles, P. N. *J. Am. Chem. Soc.* **1975**, *97*, 934.

[37] Oxygen exchange with H_2O is a general feature of polyoxometalate chemistry. See, for example: Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93 and the reviews in ref 1.

[38] Neumann, R.; Levin, M. *J. Am. Chem. Soc.* **1992**, *114*, 7278.



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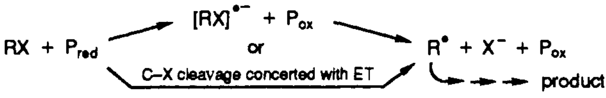
not discuss it further. The final and less than compelling argument for AT is the experimental evidence in Figure 3A showing a 68% correlation between dehalogenation by $H_2W_{10}O_{32}^{4-}$ and tri-*n*-butyl tin radicals, a model for an "authentic" AT dehalogenation (*vide supra*).

At the other end of the AT-ET mechanistic continuum for reductive carbon–halogen bond cleavage in alkyl halides is a purely ET process. Several processes have been proposed to be partially or solely ET in character including reductive dehalogenation by Co(I) species, several reduced metalloporphyrins, Cr(II) reagents, reduced cobalt dodecatungstates (reduction of polyhalogenated aliphatic compounds), aromatic radical anions, solvated electrons, and inert electrode interfaces.[13,39] The Marcus treatment (with both the reorganization energy, λ, and standard ground state redox potential, $E°(RX/RX^{\bullet-})$, or only $E°(RX/RX^{\bullet-})$ as variable parameters) has been applied in several cases.[39] A compact form of the Marcus relationship in context with Eyring transition state theory is given in eq 9 (electrostatic work term assumed to be

$$k_{obs} = 10^{11} \exp(-[(\lambda/4)(1 + \Delta G°'/\lambda)^2/RT]) \quad (9)$$

zero; $\Delta G°'$ = standard free energy driving force for the reaction).[13,39] Some of data correlate well with the Marcus expression but there are major uncertainties in the nature of electron transfer and the application of Marcus or rate-driving force relationships other than linear free energy relationships (LFER) in these studies. First, it is not clear that one requisite for rigorous application of the Marcus treatment is operable, specifically the assumption of adiabaticity in the process with an electronic interaction between the reactants and the transition state of less than 1 kcal/mol. The majority of reductive dehalogenations, and more than likely those by reduced polyoxotungstates, are irreversible processes. Furthermore, the Marcus relationship curves to which the experimental data are to be fit are difficult at best to calculate as the thermochemical data for alkyl halides is marginal and redox potentials, although extensively examined by Saveant and co-workers, are subject to considerable error if the reductions do not rigorously involve dissociative electron transfer (carbon–halogen bond cleavage concerted with addition of the electron), eq 10, bottom. Although



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adequate experimental evidence exists for short-lived but discrete anion radicals resulting from electron transfer reduction of aromatic halides ($[RX]^{\bullet-}$ in eq 10 = $ArX^{\bullet-}$)[40] or polyhalogenated alkanes,[41] the situation is not simple with common aliphatic halocarbons. Both theoretical and considerable experimental evidence has yet to unequivocally clarify whether haloalkane anion radicals, $RX^{\bullet-}$, exist for two or more molecular vibrations or not.[42]

Dehalogenation Mode 2: Catalytic Photochemical Dehalogenation of Aliphatic Halocarbons under Anaerobic Conditions. Irradiation of solutions containing $H_2W_{10}O_{32}^{4-}$, α-$HPW_{12}O_{40}^{3-}$ or other photoredox active polyoxotungstate, a sacrificial reducing agent (e.g. a primary or secondary alcohol), and halocarbon substrate results in the photocatalytic dehalogenation of the halocarbon substrate and coupled oxidation of the sacrificial reductant (e.g. alcohol to the corresponding aldehyde or ketone). An exemplary reaction is given in eq 11. Additional mode 2

$$3CCl_4 + 3(CH_3)_2CHOH + W_{10}O_{32}^{4-} + h\nu \rightarrow CHCl_3 + C_2Cl_6 + 3H^+ + 3Cl^- + 3(CH_3)_2CO + H_2W_{10}O_{32}^{4-} \quad (11)$$

reactions are summarized in Table II. The lack of a sacrificial donor (a facile reductant of the polyoxotungstate excited state) significantly decreases the product yields. Several solvents can be used, including acetonitrile, *N,N*-dimethylformamide, pure alcohol, or polar aprotic solutions of alcohol. The desirable classes of sacrificial donors in this chemistry are primary or secondary alcohols and *N,N*-dimethylformamide as all transform to products without carbon–halogen bonds. In all these cases, polyoxotungstate photooxidation generates carbon-based radicals which dehalogenate halocarbon substrate to form halohydrin-like species which readily convert to HX and nonhalogenated organic product (ketones or *N*-methylformamide).[43] The use of other classes of compounds, including hydrocarbons, as sacrificial reductants for the polyoxotungstate excited state leads to carbon-based radicals which dehalogenate the halocarbon substrate but simply form other undesirable carbon–halogen bonds. The stoichiometry of eq 11 and the processes in Table II are difficult to quantify as three types of products are susceptible to further transformation under the reaction conditions: the initial dehalogenated products ($CHCl_3$ and C_2Cl_6 in the case of CCl_4 reduction in eq 11), the oxidized form of the sacrificial reductant (e.g. $(CH_3)_2CO$ in eq 11), and inorganic halide (e.g. Cl^- in eq 11). The possible oxidation of Cl^- to ClO_4^-, ClO_3^-, or ClO^- prompted us to examine photochemical and dark control reactions between the latter chlorine oxyanions and mono- or polyhaloalkanes (e.g. Table II, eqs 19–23). No dehalogenation was seen in any of these control reactions.

This mode 2 dehalogenation chemistry is based on combining in one pot two previously established processes, the catalytic photochemical generation of carbon-centered radicals, R•, by polyoxometalates (illustrated in eqs 12–14 using decatungstate as an exemplary polyoxometalate)[5–8] and the well-known dehalogenation of aliphatic halocarbons by such radicals, e.g. eq 15.[18] Equation 15 has often been used to trap carbon-centered radicals.[44,45]

$$W_{10}O_{32}^{4-} + h\nu \rightarrow W_{10}O_{32}^{4-*} \quad (12)$$

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[39] Review: Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

[40] Haloarene anion radicals have half-lives on the ns time scale and the $ArX/ArX^{\bullet-}$ potentials have been measured electrochemically: Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

[41] (a) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1973**, 577. (b) Hasegawa, A.; Williams, F. *Chem. Phys. Lett.* **1977**, *46*, 66. (c) Brickenstein, E. Kh.; Khairutdinov, R. F. *Chem. Phys. Lett.* **1985**, *115*, 176.

[42] (a) Canadell, E.; Karofiloglou, P.; Salem, L. *J. Am. Chem. Soc.* **1980**, *102*, 855. (b) Clark, T. *J. Chem. Soc., Chem. Commun.* **1981**, 515. (c) Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys. Lett.* **1979**, *65*, 434. See also references in footnotes 12, 13, and 39.

[43] Contrary to general trends in bonding and group homolytic bond dissociation energies, the *N*-methyl and not the aldehyde-type carbon–hydrogen bonds of *N,N*-dimethylformamide have the weakest energies and likely the greatest reactivities toward radical species (personal correspondence, Eberson, L.).

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[45] The preponderance of the experimental evidence argues that reactions between carbon-based radicals and halocarbons proceed by atom abstraction and not by initial electron transfer, halide ion abstraction, or other mechanisms.[18]

Table II. Anaerobic Photochemical (Mode 2) Dehalogenation of Organic Halides by Polyoxometalates[a]

	polyoxometalate[b]	substrate	solvent	mole ratio[c]	% conversion[d] (*hν*, h)
1.	$Q_4W_{10}O_{32}$	CCl_4	CH_3CN	50.0	4.5 (12)
2.	$Q_4W_{10}O_{32}$	1-$C_6H_{13}Br$	CH_3CN	50.0	4.5 (12)
3.	$Q_4W_{10}O_{32}$	*c*-$C_6H_{11}Br$	CH_3CN	60.0	4.4 (12)
4.	$Q_4W_{10}O_{32}$	CBr_4	CH_3CN	50.0	11 (15)
5.	α-$H_3PW_{12}O_{40}$	CBr_4	CH_3CN	50.0	8.3 (15)
6.	$Q_4W_{10}O_{32}$	1-$C_5H_{11}Cl$	CH_3CN	50.0	2.8 (12)
7.	$Q_4W_{10}O_{32}$	C_6H_5Cl	CH_3CN	70.0	0 (15)
8.	$Q_4W_{10}O_{32}$	C_6H_5Cl	DMF[e]	70.0	0 (12)
9.	$Q_4W_{10}O_{32}$	C_6HCl_5	DMF	50.0	0 (12)
10.	$Q_4W_{10}O_{32}$	C_6HCl_5	DMF/ROH[f]	50.0	13 (8)
11.	$Q_4W_{10}O_{32}$	1-$C_5H_{11}Cl$	DMF/ROH	50.0	19 (12)
12.	$Na_4W_{10}O_{32}$	CCl_4	DMF/ROH	50.0	98 (12)
13.	$Na_4W_{10}O_{32}$	CCl_4	CH_3CN/ROH	70.0	52 (7)
14.	$Na_4W_{10}O_{32}$	CCl_4	CH_3CN/R'OH[g]	50.0	45 (12)
15.	$Na_4W_{10}O_{32}$[h]	CCl_4	2-C_3H_7OH	50.0	74 (12)
16.	$Na_4W_{10}O_{32}$[h]	CCl_4	C_2H_5OH	70.0	66 (8)
17.	$Q_4W_{10}O_{32}$[h]	CCl_4	C_2H_5OH	60.0	61 (8)
18.	α-$H_3PW_{12}O_{40}$	CCl_4	C_2H_5OH	50.0	42 (12)
19.	$QClO_4$	C_6H_5Cl	CH_3CN	2.0	0 (12)
20.	$QClO_4$	*c*-$C_6H_{11}Cl$	CH_3CN	5.0	0 (12)
21.	$QClO_4$	CCl_4	CH_3CN	5.0	0 (12)
22.	$QClO_3$	*c*-$C_6H_{11}Cl$	CH_3CN	5.0	0 (12)
23.	$QClO_3$	CCl_4	CH_3CN	5.0	0 (12)

[a] Sample irradiated in 25-mL Schlenk flasks under 100% argon using 1000-W high-pressure Hg lamp at 25 ± 0.5 °C. [b] Q = tetra-*n*-butylammonium ion; concentration of polyoxotungstate = $\sim 2 \times 10^{-3}$ M in all reactions, concentration of perchlorate or chlorate in reactions 19–23: ~0.3 M. [c] Moles of substrate/moles of initial polyoxotungstate. [d] [1 − (moles of substrate at the end of the reaction/moles of substrate initially)] × 100. [e] DMF = *N*,*N*-dimethylformamide. [f] ROH = 0.2 M 2-C_3H_7OH. [g] R'OH = 0.2 M 2-C_4H_9OH. [h] Catalyst partially soluble.

$$W_{10}O_{32}^{4-*} + RH \rightarrow W_{10}O_{32}^{5-} + R^{\bullet} + H^{+} \qquad (13)$$

$$W_{10}O_{32}^{5-} + R^{\bullet} + H^{+} \rightarrow \text{several investigated processes to known products}^{5-8} \qquad (14)$$

(where RH = sacrificial or terminal organic reductant such as primary or secondary alcohols in this chemistry)

$$R^{\bullet} + CCl_4 \rightarrow RCl + CCl_3^{\bullet} \qquad (15)$$

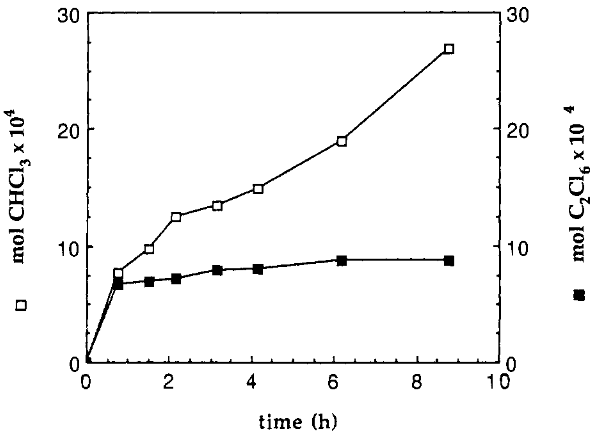

Figure 4. Time dependence of evolution of the only significant products, $CHCl_3$, the reduction product, and C_2Cl_6, the radical coupling product, in photocatalytic (mode 2) dehalogenation of CCl_4 by $Q_4W_{10}O_{32}$. $[W_{10}O_{32}^{4-}]$ = 4 mM; $[CCl_4]$ = 160 mM; [2-C_3H_7OH] = 110 mM; *T* = 25 ± 0.5 °C.

The rate law for eq 11 at low conversions is variable order in decatungstate (first order under optically dilute conditions and zero order under optically dense conditions; Figure S2), first order in light intensity consistent with a monophotonic process (Figure S3), and fractional order in both 2-propanol (Figure S4) and CCl_4 (Figure S5). Although the products and rate behavior are consistent with eqs 12–15 with a rate limiting or partly rate limiting eq 15 as the dominant mechanism for eq 11, the time dependence of the formation of the two principal organic products given in Figure 4 clarifies another important mechanistic feature in this mode 2 dehalogenation chemistry, one operable late in the reaction and after the rate limiting step. Whereas the reduction product, $CHCl_3$, and the radical dimerization product, C_2Cl_6, are generated in similar quantities at early reaction times, the yield of C_2Cl_6 stays relatively constant while the yield of $CHCl_3$ increases considerably at longer reaction times. These data are consistent with intermediate $CCl_3^{\bullet}$ radicals being reduced by reduced decatungstate (or, in general in such reactions, by reduced polyoxotungstates, HP_{red}) to the corresponding carbanions, CCl_3^-, which are then rapidly protonated to form $CHCl_3$, eq 16. Previous

$$CCl_3^{\bullet} + HP_{red} \rightarrow CHCl_3 + P_{ox} \qquad (16)$$

recent work has established that aliphatic radicals, far less oxidizing than $CCl_3^{\bullet}$, can be reduced to carbanions by reduced decatungstates.[7] A substantiation of the validity of eq 16 is that the ratio $[CHCl_3]/[C_2Cl_6]$ parallels the concentration of the reduced decatungstates: at early times little or no $W_{10}O_{32}^{5-}$ or $W_{10}O_{32}^{6-}$ is present while at late reaction times nearly all the decatungstate is reduced. Finally the relative rate of mode 1 (reduction by reduced polyoxotungstate) to mode 2 (reduction by photocatalytically generated intermediate carbon-based radicals) under the conditions where both are operable (mode 2 conditions) was assessed by initial rate kinetics (Figure S6 in supplementary material). The ratio (rate of mode 1)/(rate of mode 2) is ~15. Mode 2 is clearly dominant yet mode 1 is large enough even at fairly early reaction times to contribute to the observed complexity in the overall rate behavior of the mode 2 chemistry.

Dehalogenation Mode 3: Catalytic Photochemical Dehalogenation of Aliphatic Halocarbons under Aerobic Conditions. Addition of air or O_2 to the mode 2 reactions, with or without alcohol present, results in more extensive and more rapid dehalogenation of halocarbons. Exemplary reactions are given in Table III. Dehalogenation in some cases is satisfactory in a practical sense—effectively quantitative dehalogenation is achieved. The rationale of introducing O_2 to the system to increase dehalogenation was based on simultaneous consideration of three

Table III. Aerobic Photochemical (Mode 3) Dehalogenation of Organic Halides by Polyoxometalates in Different Solvents[a]

	P[b]	substrate	solvent	mol ratio[c]	% conversion[d] after 4 h	% conversion ($h\nu$ time)[d]
1.	$Na_4W_{10}O_{32}$	$EtS(CH_2)_2Cl$[e]	CH_3CN	8.0	95	99 (6.0)
2.	$Na_4W_{10}O_{32}$	1-$C_6H_{13}Br$	CH_3CN	57.0	92	99 (7.0)
3.	$Na_4W_{10}O_{32}$	1·$C_5H_{11}Cl$	CH_3CN	66.0	77	95 (12)
4.	$Na_4W_{10}O_{32}$	c-$C_6H_{11}Cl$	CH_3CN	200	74	89 (18)
5.	$Na_4W_{10}O_{32}$	$(CH_3)_3CBr$	CH_3CN	220	94	97 (18)
6.	$Na_4W_{10}O_{32}$	c-$C_6H_{11}Br$	CH_3CN	58.0	92	96 (12)
7.	$Q_4W_{10}O_{32}$	$(CH_3)_3CCl$	CH_3CN	80.0	~0	3.0 (20)
8.	$Q_4W_{10}O_{32}$	C_6H_5Cl	CH_3CN	50.0	~0	8.5 (21)
9.	$Q_4W_{10}O_{32}$	CCl_4	DMF[f]	40.0	90	100 (8.0)
10.	$Q_4W_{10}O_{32}$	CBr_4	DMF	15.0	100	100 (4.0)
11.	$Q_4W_{10}O_{32}$	$C_6H_5Cl_2$	DMF	50.0	~0	3.5 (21)
12.	$Q_4W_{10}O_{32}$	C_6HCl_5	DMF	50.0	2.8	34 (21)
13.	$Q_4W_{10}O_{32}$	CCl_4	CH_3CN	60.0	38	63 (8.0)
14.	$Na_4W_{10}O_{32}$	CBr_4	CH_3CN	80.0	45	70 (20)
15.	$Na_4W_{10}O_{32}$	$C_6H_4Br_2$	CH_3CN	80.0	~0	5.0 (20)

[a] Samples irradiated in Pyrex Schlenk flasks under an atmosphere of pure oxygen by using 1000-W high-pressure Xe arc lamp at 25 ± 0.5 °C. [b] P = polyoxotungstate; concentration of polyoxotungstate = 2.9×10^{-3} M in reaction 1; 1.7×10^{-3} M in reaction 2; 1.5×10^{-3} M in reaction 3; 1.0×10^{-3} M in reactions 4 and 5; 2.5×10^{-3} M in reactions 6–8; 2.5×10^{-3} M in reactions 9–13; and/or 4.0×10^{-3} M in reaction 14,15. [c] Moles of substrate/moles of initial $W_{10}O_{32}^{4-}$. [d] Moles of reactant halocarbon at termination of reaction/moles of initial reactant halocarbon. Final column gives conversion after the irradiation times, in h, given in parentheses. [e] Half mustard ($CH_3CH_2SCH_2CH_2Cl$). [f] DMF = *N*,*N*-dimethylformamide.

recently established experimental facts: (1) under conditions of steady state photolysis in mode 2 above, the dominant polyoxotungstates present are the reduced species, (2) these reduced complexes are readily reoxidized to the oxidized complexes by O_2 resulting in initial formation of superoxide, $O_2^{\bullet -}$, e.g. eq 17 (with ultimate formation of H_2O, eq 18), and (3) the superoxide thus formed can directly dehalogenate the halocarbon substrates by

$$H_2W_{10}O_{32}^{4-} + O_2 \rightarrow HW_{10}O_{32}^{4-} + H^+ + O_2^{\bullet -} \quad (17)$$

net final reaction:

$$H_2W_{10}O_{32}^{4-} + 1/2O_2 \rightarrow W_{10}O_{32}^{4-} + H_2O \quad (18)$$

multiple processes. The chemistry in step 3, including considerable analysis of products and mechanism, has already been reported by Sawyer and co-workers.[19] We find similar products (dehalogenated and oxygenated compounds) providing general evidence for similar dehalogenating species in the mode 3 reactions and in the Sawyer chemistry. Clearly the dominant dehalogenating species present in mode 1 (reduced polyoxotungstate) and mode 2 (carbon-based radicals and reduced polyoxotungstate) are present in mode 3. But other radical species dominate dehalogenation in mode 3, in part as eq 17 (reaction of reduced polyoxotungstates in general with O_2) is at least two orders of magnitude faster than eq 2 (reaction of reduced polyoxometalates in general with halocarbons) for most of the halocarbon substrates. Repeated attempts to obtain satisfactory and rigorous kinetics data on representative mode 3 reactions proved to be impractical as the reproducibility of all attempted experiments was always low and practical inferences of mechanism would be speculative at best without considerable rate data on such a complex system. The inherent complexity of the mode 3 reactions themselves also likely contributes to the low reproducibility of rate data.

Conclusions

(1) It has been demonstrated for the first time that redox active polyoxotungstates (such as the representative isopolytungstate, $W_{10}O_{32}^{4-}$, and the heteropolytungstate, α-$PW_{12}O_{40}^{3-}$, specifically examined here) facilitate three modes of carbon–halogen bond cleavage.

(2) The first mode involves direct dehalogenation by reduced forms of the polyoxotungstates ($H_2W_{10}O_{32}^{4-}$ and α-$HPW_{12}O_{40}^{3-}$ in this study). These reactions are fairly slow bimolecular and *thermal* in nature. The rate law, relative reactivities of substrates (primary/secondary/tertiary; polyhalogenated/monohalogenated; chlorides/bromides), structure–reactivity profiles, product distributions, and other data establish two key points about these processes: (i) intermediate alkyl radicals are important in most if not all these reactions, and (ii) carbon–halogen bond cleavage involves either electron transfer (ET), which is probably dissociative in nature, or halogen abstraction (atom transfer or AT) in the rate-limiting step (all other processes for this step can be ruled out).

(3) Dehalogenation in mode 1 can involve either oxidation of alkyl radical intermediates to carbonium ions (seen when both easily oxidized tertiary radicals and some oxidized polyoxotungstate are simultaneously present) or reduction of alkyl radical intermediates to carbanions (seen in most cases). Increasing the acidity traps more carbanion leading to higher yields of reduction product (direct replacement of the carbon–halogen bond with the carbon–hydrogen bond).

(4) The second mode involves the photochemical dehalogenation of chlorocarbons and bromocarbons by sacrificial reductants (secondary alcohols or tertiary amides which are converted to ketones and secondary amides, respectively) catalyzed by polyoxotungstates. In these processes, the sacrificial reductant is oxidized by the polyoxometalate excited state to an intermediate carbon-based radical which subsequently dehalogenates the halocarbon substrate. The reactions are catalytic in polyoxometalate and more than an order of magnitude faster than the reactions in mode 1.

(5) The third mode involves the use of polyoxometalates to catalytically generate superoxide, a well-known and effective dehalogenating agent. Dioxygen is added to the mode 2 reactions which reoxidizes the photoreduced polyoxotungstate intermediate thus forming superoxide and reforming the oxidized polyoxotungstate. While carbon–halogen bond cleavage in mode 3 is taking place by reaction with reduced polyoxotungstate, intermediate organic radicals, and superoxide, reactions of the latter dominate. Only in mode 3 is dehalogenation both relatively rapid and quite complete for most substrates (Table III).

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Supplementary Material Available: Potentiometric titration curves for the photoreduced complexes, $W_{10}O_{32}^{6-}$ and α-$PW_{12}O_{40}^{4-}$, rates studies of CCl_4 dechlorination by 2-propanol catalyzed by $W_{10}O_{32}^{4-}$, and relative rates of CCl_4 dechlorination in mode 1 and mode 2 (7 pages). Ordering information is given on any current masthead page.