Discussion

It is informative to compare the results of this study with those obtained earlier for $Cp_2Co_3(CO)_4(\mu_3\text{-}CPh)$,[4] in which it was found that an orbital interaction between the ring and bridging carbonyl completely immobilizes the phenyl group on the molecular reorientation (nanosecond) time scale (vide supra). The tumbling rate of the heterometallic cluster is quite close to that of the tricobalt complex; e.g. at 298 K, $D_\perp(FeCo_2) = 4.9\ ns^{-1}$ versus $D_\perp(Co_3) = 4.2\ ns^{-1}$.[4] This result is expected, considering the similar dimensions of the two species. In contrast, as shown in Table I and Figure 1 (lines A and B), the rate of phenyl group spinning in $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ is from 4 to 6 times more rapid than in $Cp_2Co_3(CO)_4(\mu_3\text{-}CPh)$. This shows clearly that there is a substantially lower barrier to internal rotation in the former complex.

To determine whether there is any measurable hindrance to rotation of the phenyl ring, one may compare $D_S(FeCo_2)$ to the rate of the equivalent rotation of free benzene (about its C_2 axis) in chloroform,[13] which we denote as $D_S(Bz)$. As seen in Table I and Figure 1 (lines B and C), the phenyl spinning rate in the complex is somewhat lower, by about 35%, than the rate of rotation of benzene in the same solvent. $D_S(FeCo_2)$ is also below the rotational rate found in an earlier study[3] of the complex, $Co_3(CO)_9(\mu_3\text{-}CPh)$ (points D), where, as noted above, it was found that D_S of the phenyl group is equal to that of benzene, to within experimental error, in agreement with the theoretical calculations of Schilling and Hoffmann.[6]

On the basis of the above comparisons, it appears that the replacement of $Co(CO)_3$ and a μ_3-CPh fragment with $Fe(CO)_3$ and a μ_3-PPh fragment, respectively, does induce an electronic perturbation in the metal's orbitals that leads to a small, but finite barrier to internal rotation of the capping phenyl group. However, it is clear, too, that this barrier is much smaller than that found in earlier investigations of carbonyl bridged clusters.[4,8] In addition, we must add the caveat that it is possible, but not likely, that the relatively small hindrance to ring rotation might be attributable, instead, to another effect such as preferential solvation of the phenyl group in $FeCo_2(CO)_9(\mu_3\text{-}PPh)$, although this was not seen in the previous investigation of $Co_3(CO)_9(\mu_3\text{-}CPh)$.

Further investigations of carbonyl-bridged and heterometallic species will be necessary to fully assess the factors influencing the magnitude of electronic barriers in metal carbonyl clusters.

Acknowledgment. We wish to acknowledge the Robert A. Welch Foundation [Grants B-1039 (M.G.R.) and B-657 (M.S.)] and the UNT Faculty Research Fund for support of this research and Ming-Jaw Don for the sample of $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ used in this study.

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Aerobic Photooxidation of Substituted Benzenes Catalyzed by the Tungsten Isopolyanion $[W_{10}O_{32}]^{4-}$

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Inorganic, soluble iso- and heteropolyanion oxides[1] are promising candidates for the functionalization of organic compounds. Very recent work has shown that the decatungstate anion, $[W_{10}O_{32}]^{4-}$ (W10), in particular may behave as an efficient, stable, selective photooxidation catalyst.[2-7]

Under anaerobic conditions W10 selectively promotes the dimerization of several olefins[2] and the dehydrogenation of alkanes to alkenes,[3] reoxidation of the reduced catalyst occurring at the expense of hydrogen ions. Although the yields are not particularly high, one distinct advantage of W10 is its high quantum yield efficiency, with measured values which may approach unity, when mineral acids are added to the reaction mixture.[3]

Preliminary reports[5-7] suggest that, under aerobic conditions, W10 promotes the oxidation of saturated hydrocarbons, notably branched ones containing tertiary carbon atoms. By use of a classical autoxidation mechanism, alkyl hydroperoxides or oxygenated products deriving from their further reactivity are obtained in moderate yields. No information is available concerning the related hexatungstate anion $[W_6O_{19}]^{2-}$ (W6).

Following our previous interest in this field,[8,9] we now report new results concerning the ability of W10 to catalyze the aerobic photooxidation of various alkylbenzenes. Experimental data showing W6 or its V(V)-substituted derivative to be totally inactive toward such oxidations are also presented.

Experimental Section

Materials. $[Bu_4N]_4W_{10}O_{32}$ and $[Bu_4N]_3VW_5O_{19}$ were prepared and purified according to published methods.[10,11] The synthesis of $[Bu_4N]_2W_6O_{19}$, reported in the literature,[12] was modified by using the much easier procedure given below. Commercially available alkylbenzenes (Fluka, purity ≥99%) were used as received. Acetonitrile was freshly distilled from CaH_2 under a stream of prepurified nitrogen.

Measurements. Elemental analyses were performed by H. Malissa Analitische Laboratorium, Elbach, FRG. IR and electronic spectra were recorded, respectively, on Perkin-Elmer 983G and Perkin-Elmer 330 spectrophotometers. Qualitative and quantitative product analysis was accomplished by GC, eventually coinjecting authentic samples, using a Perkin-Elmer 8500 gas cromatograph equipped with a packed column (length 2 m, filling 5% Carbowax on Chromosorb W80/100) and with an HP 3390A integrator.

Synthesis of $[Bu_4N]_2W_6O_{19}$. $Na_2WO_4\cdot 2H_2O$ (6.0 g, 18.0 mmol) was dissolved in boiling CH_3CN (150 mL). Acidification was performed by addition of a boiling solution of HCl 12 N (2.5 mL) in water (200 mL). After a few minutes of stirring, Bu_4NCl (1.78 g, 6.0 mmol) dissolved in water (20 mL) was added dropwise to the pale yellow solution. After cooling, the white, crystalline precpitate was filtered out, washed with ethanol and ether, and crystallized from a small amount of CH_3CN (5 mL). Yield: 2.29 g (41%). Anal. Calcd for $C_{32}H_{72}N_2W_6O_{19}$: C, 20.31; H, 3.84; N, 1.48; W, 58.30. Found: C, 20.26; H, 3.85; N, 1.45; W, 58.05. UV-vis (CH_3CN): λ_{max} 280 nm (ϵ $1.18 \times 10^4\ dm^3/(mol\cdot cm)$).

Photochemical Oxidations. Aerobic reactions were performed in a homemade immersion reactor by dissolving the substrate (12.5 mmol) and the required amount of catalyst in 100 mL of CH_3CN. A 125-W high-pressure mercury lamp, in conjunction with a cold-water Pyrex cutoff filter ($\lambda \geq 320$ nm), was used as a source of irradiation. The reaction solutions were kept under a constant, slight overpressure of pure dry oxygen or air and thoroughly stirred and thermostated at 25 °C (if not otherwise stated). Sampling and analyses were performed at 1- and 2-h intervals.

Results and Discussion

This note describes the aerobic, catalytic photooxidation of various alkylbenzenes in the presence of $[W_{10}O_{32}]^{4-}$ and related tungsten isopolyanions. The basic reaction investigated is

$$PhR + O_2 \xrightarrow[h\nu,\ CH_3CN,\ 25\ ^\circ C]{POA\ catalyst} \text{carbonyl derivative} + \text{carboxylic acid} + \text{minor products}$$

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Table I. Photooxidation of Different Alkylaromatic Hydrocarbons Catalyzed by $[Bu_4N]_4W_{10}O_{32}$ in CH_3CN at 25 °C[a]

			8 h		24 h		
run	substrate	product	% conversion	% yield	% conversion	% yield	t/h[b]
1	*p*-xylene	*p*-toluic acid	90	82	100	91	17
2	toluene	benzoic acid	58	46	92	90	10
3	cumene	acetophenone + 2-phenylpropan-2-ol	60	46	92	76	11
4	ethylbenzene	acetophenone	65	45	93	71	11
5	ethylbenzene[c]	acetophenone	6	3	28	15	1
6	ethylbenzene[d]	acetophenone	41	27	90	57	6
7[e]	ethylbenzene[d]	acetophenone	41	28	70	49	55
8[e]	ethylbenzene	acetophenone	7	5	23	15	110

[a] Unless otherwise stated, reactions were run under pure oxygen. The substrate concentration was 0.125 mol/dm^3, and the substrate:catalyst molar ratio, 125. Minor products were analyzed only in the case of EtPh, which shows the lowest selectivity. Initially, PhCHO and $PhCHOHCH_3$ were detected. At later stages, their concentration decreased and PhCOOH was formed as the only detectable byproduct. [b] t/h was calculated after 6 h, i.e. in the linear region of the conversion plot, and is given as the moles of the converted substrate divided by the moles of catalyst and by the time. [c] Catalyst used: $[Bu_4N]_3PW_{12}O_{40}$. Data were taken from ref 8. [d] Reaction run under air. [e] *R* values: 1000 (run 7) and 10000 (run 8).

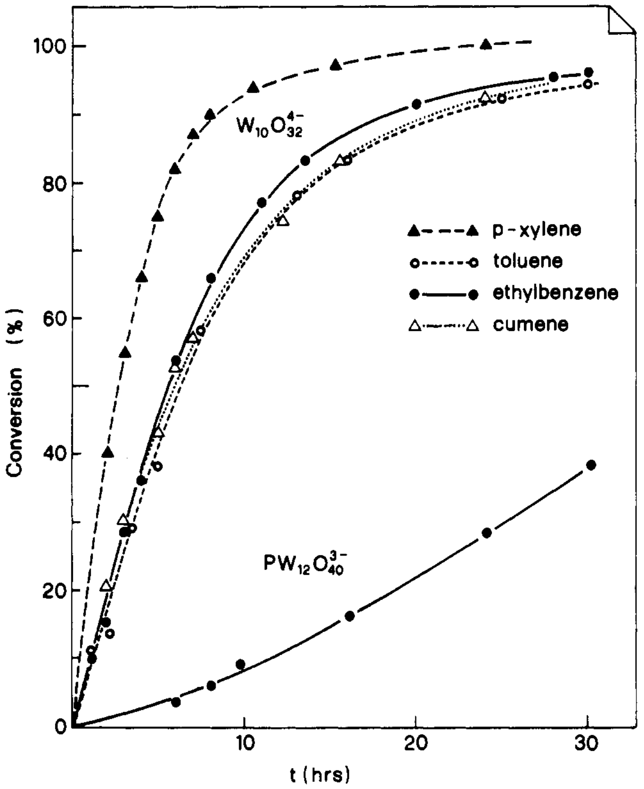

Figure 1. Photochemical oxidation of alkylaromatic hydrocarbons catalyzed by the polyoxometalate $[Bu_4N]_4W_{10}O_{32}$ in CH_3CN. Results obtained by using $(Bu_4N)_3PW_{12}O_{40}$ are reported for comparison from ref 8. Substrate concentration = 0.125 mol/dm^3; catalyst concentration = 1 × 10^{-3} mol/dm^3; *T* = 25 °C.

Figure 1 summarizes the essential results of the reaction. Quantitative data are given in Table I. Unless otherwise stated, molar concentrations for the substrate and the W10 catalyst were respectively 0.125 mol/dm^3 and 1 × 10^{-3} mol/dm^3, the molar ratio *R* being 125.

Under these conditions, almost complete oxidation of *p*-xylene (94%) occurs in about 10 h, the yield of *p*-toluic acid being 82% and the selectivity of the reaction 87%. The remaining part of the reacted substrate is recovered as roughly equimolar amounts of *p*-tolualdehyde and terephthalic acid (ca. 6% each). The almost insoluble organic acid directly precipitates from the reaction mixture in analytically pure form. The other three hydrocarbons, toluene, ethylbenzene, and cumene, show a much slower reaction rate. Their percent conversion is about 70% after 10 h and reaches 92%–94% only after 24 h of irradiation. A comparison of the different t/h (number of turnovers per hour; see Table I) measured in the linear region of the reaction (6 h) and defined as the moles of total products formed per mole of catalyst per hour, clearly gives a quantitative indication of the different rates. As far as the products are concerned they are typical of a classical radical-chain autoxidation mechanism. Benzoic acid and acetophenone are the oxidation products of toluene and ethylbenzene, the selectivities being 98% and 76%, respectively. In the case of cumene, cleavage of the carbon–carbon bond is possible and a roughly equimolar mixture (40:60) of acetophenone and the tertiary alcohol 2-phenylpropan-2-ol is obtained.

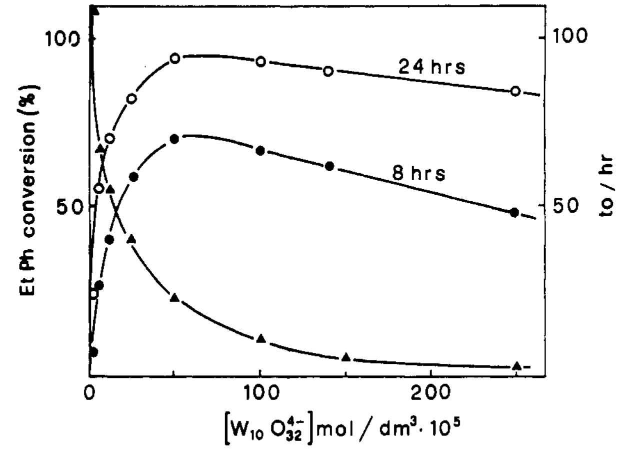

Figure 2. Effect of catalyst concentration on the conversion rate of ethylbenzene after 8 (●) or 24 (○) h of reaction. The number of turnovers per hour is also reported (▲). Substrate concentration = 0.125 mol/dm^{-3}; *T* = 25 °C. The molar ratio between substrate and catalyst (*R*) ranges from 50 to 10000.

Consumption of the substrate slows down the oxidation reactions after 6–8 h. Therefore, tests of the catalytic stability were performed at much higher *R* values (*R* = substrate:catalyst molar ratio), up to 10000. Under these conditions, the reaction continues linearly for at least 30 h, starting at a rate of ca. 110 t/h and going to completion over 2500 turnovers. After this point the reaction rate slows down, possibly indicating catalyst deterioration. However, spectroscopic check proved to be difficult, owing to the onset of high-intensity absorption bands from the products which, after some time, are present at concentrations much larger than the catalyst (W10 and acetophenone, for instance, absorb at 323 and 240 nm, respectively, with similar extinction coefficients 1.33 × 10^4 and 1.49 × 10^4 dm^3/(mol·cm)).

With the aim of optimizing the above processes, some additional experiments have been carried out. We have tested the dependence of the oxidation rate upon *R* values, absolute concentrations, and oxygen pressure.

Reactions have been performed with *R* values ranging from 50 to 10000, still using a fixed concentration of the test substrate ethylbenzene, 0.125 mol/dm^3. Figure 2 shows that, upon an increase in the catalyst concentration, the reaction rate increases and goes through a maximum (*R* ≈ 250), after which a linear decrease in the reaction rate is observed. However, such rate depends on the actual concentration of the active catalyst present in its excited state, [W10*], which in turn is limited by the irradiation conditions used. Therefore, a possible explanation for the above result is that increase in [W10], above some limiting value, may result in bimolecular quenching of W10* by another ground-state W10 molecule, thus reducing the actual amount of decatungstate present in its, catalytically active, excited state.

Figure 2 also shows that the number of turnovers per hour sharply decreases as a function of the catalyst concentration. The reciprocal of t/h can be satisfactorily fitted as a linear function of [W10]. As a consequence, both the conversion of substrate and the formation of the oxygenated main product are essentially constant and independent on the amount of catalyst in a large interval of [W10] (from 2.5×10^{-3} to 2.5×10^{-4} mol/dm^3).

Use of fixed *R* values but larger absolute concentrations of both substrate and catalyst (up to 4 times) strongly slows down the reaction rate. Likewise, considerable lower yields are obtained if the standard EtPh oxidation reaction is run under air ($p(O_2) \approx 20$ kPa) instead of under pure oxygen ($p(O_2) \approx 100$ kPa; compare runs 4 and 6 in Table I). Apparently, the concentration of O_2 in CH_3CN (approximately 10^{-2} mol/dm^3 at 25 °C and 1 atm) is a limiting factor that does not permit full exploitation of the catalyst efficiency. This is further supported by the fact that runs 4 and 6 show, after 24 h, similar percent conversions but considerably different yields of acetophenone. Possibly the lower O_2 concentration and the less efficient formation of benzylperoxy radicals allow the initially formed benzyl-type radicals to follow alternative reaction paths with formation of different final products.

Oxidation tests run in the presence of $[W_6O_{19}]^{2-}$ or $[VW_5O_{19}]^{3-}$ showed these two polyanions to be completely inactive. In the case of W6, this may be ascribed to its absorption maximum being shifted toward the UV region (λ 280 nm, ϵ 1.18×10^4 dm^3/(mol·cm)). In spite of this, we would have expected a small but measurable activity, due to the fact that the absorption manifold of W6 has a tail extending nearly into the visible region. Such behavior has been previously[8] found for $[PW_{12}O_{40}]^{3-}$, which absorbs at even lower wavelengths, 265 nm. The complete inactivity of W6 suggests that the unique catalytic properties of W10 have to be ascribed both to its optical spectrum being shifted toward the visible region (λ 323 nm, ϵ 1.33×10^4 dm^3/(mol·cm)) and to its ability to interact strongly with organic substrates.

The inactivity of the V-substituted polyanion, which is a significantly stronger oxidation and exhibits visible absorption, may be also interpreted in terms of its reduced capability to interact electronically with the organic substrate. In fact, the extra negative charge carried by VW5 may weaken the electrostatic interaction with the electron-rich substrates, leading to poorer precomplexation and less efficient electron exchange upon photoactivation.[13]

The last point to be stressed in this preliminary report is the much higher reactivity shown by *p*-xylene compared to the other three hydrocarbons, which show closely similar behaviors. *p*-Xylene has an ionization potential (IP) that is about 0.3 eV lower than the IP of monosubstituted benzenes.[14] A likely possibility is to assume that the first oxidation step is a direct electron transfer from the organic substrate to the polyanion catalyst, with formation of the aromatic cation radical. Subsequent loss of an α-proton gives a benzyl radical that immediately reacts with molecular oxygen to yield the peroxide radical. Similar mechanisms have been reported for the oxidation of alkylbenzenes in the presence of high concentrations of cobalt catalysts.[15] ESR experiments, to check the presence of the aromatic cation radical, are planned.

Registry No. $(Bu_4N)_4W_{10}O_{32}$, 68109-03-5; $(Bu_4N)_3VW_5O_{19}$, 11087-54-0; $(Bu_4N)_2W_6O_{19}$, 12329-10-1; *p*-xylene, 106-42-3; toluene, 108-88-3; cumene, 98-82-8; ethylbenzene, 100-41-4; *p*-toluic acid, 99-94-5; benzoic acid, 65-85-0; acetophenone, 98-86-2; 2-phenyl-2-propanol, 617-94-7; *p*-tolualdehyde, 104-87-0; terephthalic acid, 100-21-0.

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Additions and Corrections

1990, Volume 29

Andrew G. Sykes and Kent R. Mann*: X-ray Crystal Structure and Homonuclear ^{31}P–^{31}P δ/J-Resolved NMR Spectroscopic Studies of $[AgIr_2(dimen)_4(PPh_3)_2](PF_6)_3$. Observation of a Statistical Mixture of "Head/Tail" Isomers.

Page 4452. Figures 4 and 5 have been interchanged. The captions are correct.—Kent R. Mann

B. G. Gafford, R. E. Marsh, W. P. Schaefer, J. H. Zhang, C. J. O'Connor, and R. A. Holwerda*: Synthesis, Structure, and Physical Properties of (μ-Oxo)(μ-carboxylato)bis{(tris(2-pyridylmethyl)amine)chromium(III)} Complexes.

Page 4657. In the left column, the first complete sentence should read as follows: According to the Glerup–Hodgson–Pedersen model,[21] the singlet–triplet gap ($-2J$) in hydroxo- and oxo-bridged Cr(III) dimers should enlarge with increasing M–O–M (ϕ) and decreasing dihedral (θ, bridging OH^-) angles.—R. A. Holwerda