radiation 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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(13) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347.

(14) Howe, I.; Williams, D. H.; Bowen, R. D. *Mass Spectrometry, Principles and Applications*; McGraw-Hill: New York, 1981.

(15) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

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