The blue crystals dissolve in THF to give a blue solution which turns green in ~10 min. No homogeneous green product has yet been isolated. The blue crystals were shown by X-ray crystallography to be $Na_4(TMEDA)_4W_2Cl_8$; in THF solution at 0 °C the 600-nm band with ϵ 1600 was observed, and a satisfactory elemental analysis was obtained.[12]

Of 20 well-formed, single, blue-green, dichroic crystals, mounted and sealed in capillaries under nitrogen, only two were sufficiently stable (ca. 50% loss of intensity during ca. 48 h of exposure to X-rays) to provide sets of diffraction data. With these data the structure was solved and refined.[13-15] The two independent, centrosymmetric $[W_2Cl_8]^{4-}$ ions are essentially equivalent. The one residing at the origin is depicted, along with its neighboring Na^+ ions, in Figure 1. The key dimensions are listed in Table I. These may be compared with corresponding dimensions of the $[Mo_2Cl_8]^{4-}$ ion,[16] in which have been found the following: Mo–Mo, 2.134–2.150 Å; Mo–Cl, 2.45–2.47 Å (mean values); Mo′–Mo–Cl, 105.0 ± 0.2°. The W–W distance is thus about 0.11–0.13 Å longer than the Mo–Mo bond and the mean W–Cl bond is slightly (ca. 0.02 Å) shorter than the Mo–Cl bond, both of which were anticipated in an earlier discussion.[17]

As indicated in Figure 1 the sodium ions are closely associated with the $[W_2Cl_8]^{4-}$ ions so that one Na^+ ion caps each vertical face of the rectangular prism having on its 4-fold axis the W_2^{4+} unit.[18] The $Na^+\cdots Cl$ distances range from 2.815 to 2.902 Å, with a mean value of 2.85 [1] Å. One TMEDA molecule is coordinated through both N atoms to each sodium ion, with Na–N distances ranging from 2.47 to 2.59 Å and having a mean value of 2.52 [2] Å.

Acknowledgment. We are grateful to the National Science Foundation for financial support at both institutions, and L.G.S. acknowledges a postgraduate scholarship from the Natural Sciences and Engineering Research Council of Canada.

Registry No. WCl_4, 13470-13-8; $W_2Cl_6(THF)_4$, 77479-88-0; $Na_4W_2Cl_8$, 83232-08-0; $Na_4(TMEDA)_4W_2Cl_8$, 83232-09-1.

Supplementary Material Available: Table S1, crystallographic data and data collection parameters; Table S2, positional parameters and their estimated standard deviations for $Na_4(TMEDA)_4W_2Cl_8$; Table S3, thermal parameters (*B*'s) and their estimated standard deviations for $Na_4(TMEDA)_4W_2Cl_8$; Table S4, observed and calculated structure factors for $Na_4(TMEDA)_4W_2Cl_8$; Table S5, bond distances and bond angles in $Na_4(TMEDA)_4W_2Cl_8$ (37 pages). Ordering information is given on any current masthead page.

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(12) Anal. Calcd for $WC_{12}H_{32}Cl_4Na_2N_4$: C, 23.86; H, 5.34; N, 9.28; Cl, 23.48. Found: C, 23.77, H, 5.30; N, 8.96; Cl, 23.09.

(13) Data were collected on an Enraf-Nonius CAD-4 diffractometer at 22 °C following conventional procedures.[14] The space group is $P\bar{1}$ with unit cell dimensions $a = 11.907$ (3) Å, $b = 15.462$ (2) Å, $c = 13.640$ (1) Å, $\alpha = 89.50$ (1)°, $\beta = 98.80$ (1)°, $\gamma = 90.30$ (2)°, $V = 2482$ (1) Å^3, $Z = 2$. Full details of the data collection and refinement are available in Table S1 (supplementary material). Data were corrected for Lorentz and polarization effects and for absorption by the empirical ψ-scan method. Data for the two crystals were merged by using approximately 500 equivalent reflections by the method of Rae and Blake.[15] All calculations were performed on a PDP 11/60 computer at B. A. Frenz and Associates, College Station, TX. The positions of the two independent tungsten atoms were obtained from a Patterson function and indicate that $[W_2Cl_8]^{4-}$ units are located on inversion centers at 0,0,0 and $^1/_2$, $^1/_2$, $^1/_2$. All other non-hydrogen atoms were found in a series of alternating difference maps and least-squares refinements. In the final refinement cycles hydrogen atoms were omitted, carbon atoms were refined isotropically, and all other atoms were refined anisotropically, giving final residuals of $R_1 = 0.076$ and $R_2 = 0.095$, and the largest shift/error ratio in any parameter was 0.04. The only peaks above random noise in the final difference map were three within <1 Å of the tungsten atoms. Several attempts to refine the structure in monoclinic space groups gave inferior results. The final positional and thermal parameters and a list of structure factors are available as supplementary material, Tables S2, S3, and S4, respectively.

(14) See, for example: Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudaroski, R. *Inorg. Chem.* **1982**, *21*, 1656.

(15) Rae, A. D.; Blake, A. B. *Acta Crystallogr.* **1966**, *20*, 586.

(16) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7, 2698; **1970**, *9*, 346.

(17) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(18) In this structure no evidence was found for any significant (>1%) secondary orientation of the W_2^{4+} unit in the Cl_8 quasi-cube, though this sort of disorder is rather common (cf. ref 1, pp 344–347) in such compounds. Perhaps the proximity of the Na^+ ions on all four vertical faces repells the positively charged tungsten atoms from the positions they would have in one of the secondary orientations.

Novel Catalytic Oxidations of Terminal Olefins by Cobalt(II)-Schiff Base Complexes

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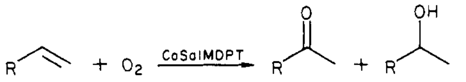
Received February 26, 1982

We report the selective catalytic oxidation of terminal olefins by molecular oxygen to the corresponding 2-ketone and 2-alcohol by using CoSalMDPT[1] complexes (reaction 1). Experiments were conducted to rule out the possibility of a free radical initiated autoxidation mechanism. The results of these experiments and further details concerning this novel reaction are reported here.



(1)

The oxidation of linear olefins by O_2 to produce ketones has been reported for a number of homogeneous transition-metal catalysts.[2] The $RhCl_3/Cu(II)$ catalyst[3] is particularly efficient and selective. Palladium(II)–copper(II) catalyst mixtures readily oxidize linear olefins via the well-known Wacker mechanism.[4] Attempts at oxidizing linear olefins with first-row transition-metal catalysts usually have resulted in reaction products typical of autoxidations,[5] which include a high degree of oxidized polymer as well as cleavage products.

CoSalMDPT catalyzes the oxidation of terminal olefins (for example, 1-hexene, 3-methyl-1-hexene, styrene, and 3-buten-1-ol) to the methyl ketone and 2-alcohol. The olefin substrate chosen to determine additional reaction parameters[6] was 1-hexene. A plot of the production of 2-hexanone at various temperatures is shown in Figure 1. The O_2 uptake correlates with the amount of 2-hexanone and 2-hexanol produced, indicating a nearly stoichiometric oxidation of 1-hexene. Polymer formation is not observed. When ethanol is used as solvent, acetaldehyde is observed in the final reaction mixture. A study of the reaction rates shows an approximate first-order dependence on cobalt concentration and 1-hexene concentration (experiments 1–4 in Table I). A zero-order dependence on O_2 pressure is observed in the 30–90-psi range studied.

In order to understand metal-catalyzed oxidations, it is always necessary to consider the possibility of the very common free radical initiated autoxidation[7] mechanism. Thus, upon discovery

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* To whom correspondence should be addressed at the University of Florida.

(1) CoSalMDPT = cobalt(II) bis(salicylidene-γ-iminopropyl)methylamine.

(2) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272.

(3) Mimoun, H.; Perez Machirant, M. M.; Sêe de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437.

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(6) All catalytic reactions were conducted in Parr pressure bottles submerged in a temperature-controlled oil bath. Besides monitoring oxygen consumption, 0.2 mL aliquots of the reaction mixture were withdrawn at various time intervals and analyzed by GC. 2-Octanone was added as an internal standard. The concentration of 2-hexanone plus 2-hexanol was calculated from a calibration curve.

Table I. Oxidation of 1-Hexene Catalyzed by CoSalMDPT

expt no.	solvent and additive	additive, mmol	CoSalMDPT, mmol	1-hexene, mmol	temp, °C	initial rate[a]	final 2-hexanone, mmol	final 2-hexanol, mmol
1	ethanol solvent[b]		0.24	39	60	0.9	2.7	1.8
2	ethanol solvent		0.49	39	60	1.7	4.7	3.1
3	ethanol solvent		0.73	39	60	2.8	6.1	4.1
4	ethanol solvent		0.73	19	60	1.4	4.8	3.3
5	ethanol solvent		0.73	39	70	4.3	6.7	4.3
6	ethanol solvent, H_2O added	55.6	0.73	39	70	1.0	3.9	3.7
7	ethanol solvent, $HClO_4$ added	1.4	0.73	39	70	0	0	0
8	1:1 ethanol-benzene		0.73	39	70	0.3	2.3	1.4
9	1:1[c] ethanol-isopropanol		0.73	40	60	0.9	6.3	4.7
10	1:1 ethanol-benzene, 2,6-di-*tert*-butyl-*p*-cresol added	1.0	0.73	39	70	0.4	2.1	1.3
11	1:1 ethanol-benzene, 2,6-di-*tert*-butyl-*p*-cresol added	20.0	0.73	39	70	0.1	0.4	0.3

[a] Rate = (mmol of 2-hexanone + mmol of 2-hexanol)/hour, taken from maximum slopes. [b] Reaction conditions: 45 mL of solvent; 80 psi of O_2 pressure; 1 mL of 2.29 M 2-octanone in EtOH added as an internal GC standard. [c] Reaction conditions: 50 mL of solvent; 80 psi of O_2 pressure; 0.28 mL of 2-octanone added as an internal GC standard.

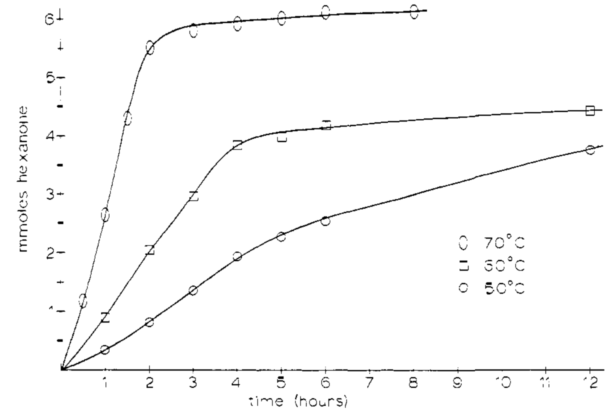

Figure 1. Production of 2-hexanone at various temperatures. All reactions were conducted in 45 mL of ethanol, with 5.0 mL of 1-hexene, 0.300 g (7.32 × 10^{-4} mol) of CoSalMDPT, and 1 mL of 2.29 M 2-octanone, at 80 psi of O_2.

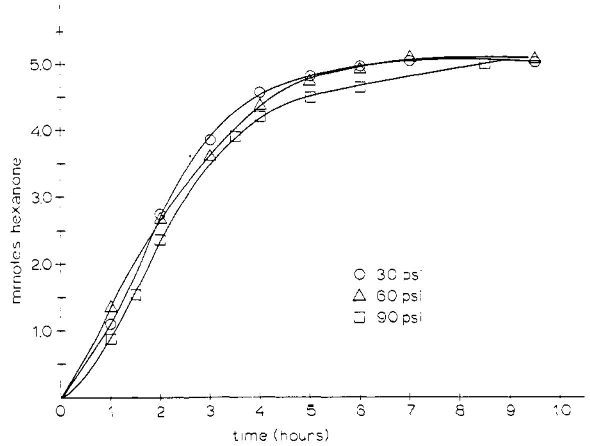

Figure 2. Production of 2-hexanone at various O_2 pressures. All reactions were conducted in 45 mL of ethanol with 5.0 mL of 1-hexene, 0.300 g of CoSalMDPT, and 1.0 mL of 2.29 M 2 octanone, at 60 °C.

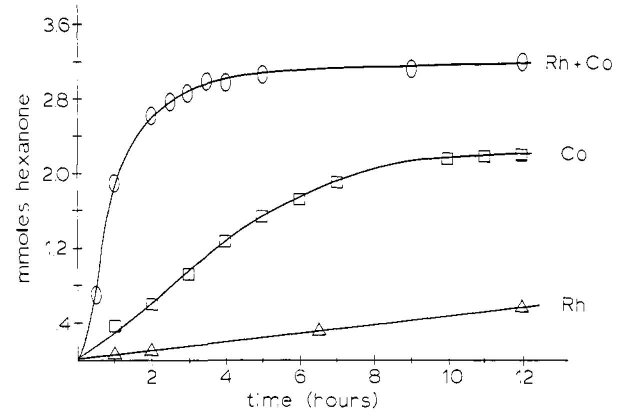

Figure 3. Synergistic enhancement of the production of 2-hexanone by the addition of $RhCl(PPh_3)_3$ to a CoSalMDPT-catalyzed reaction. 1:1 benzene–ethanol solvent, otherwise typical conditions.

of this reaction, our initial goal was to determine if this is the role played by the metal complex.

The following experimental data suggest that this unusual reaction proceeds by a mechanism other than autoxidation:

1. The reaction is remarkably solvent dependent. This reaction does not occur in benzene, *tert*-butyl alcohol or isopropyl alcohol. It does occur in methanol, ethanol, and 1:1 mixtures both of benzene–ethanol and isopropyl alcohol–ethanol. A comparison of the reaction rates and turnovers in ethanol, in a 1:1 (v/v) ethanol–benzene solvent and in a 1:1 (v/v) ethanol-isopropyl alcohol solvent, is given in Table I (experiments 5,8, and 9).
2. In the range studied (30–90 psi), the reaction rate is independent of O_2 pressure, as shown in Figure 2.
3. A long induction period is not observed (see either Figure 1 or 2). Autoxidation rates are characterized by long induction periods resulting from a free-radical-initiated process.
4. The CoSalMDPT catalyst demonstrates some substrate selectivity, oxidizing linear olefins but surprisingly not cyclohexene. However, styrene, a difficult substrate to oxidize with common autoxidation catalysts since it contains no allylic hydrogens, is oxidized at approximately the same rate as 1-hexene in our system.
5. The addition of a free-radical trap does not stop 1-hexene oxidation nor does it lead to a long induction period. Rates are decreased due to a competitive oxidation of the 2,6-disubstituted phenol by the cobalt catalyst,[8] but nevertheless, simultaneous oxidation of 1-hexene occurred.

We have also observed that no reaction occurs in the presence of dilute acid. The 2-hexanol product is not oxidized to 2-hexanone under reaction conditions. When H_2O_2 and argon are substituted for molecular oxygen, 2-hexanone and 2-hexanol are produced catalytically. Addition of peracetic acid to an attempted oxidation in isopropyl alcohol led to no significant reaction. Another interesting observation is a synergistic enhancement of the reaction rate with the addition of other transition-metal catalysts. The best example of this is demonstrated by the $RhCl(PPh_3)_3$–CoSalMDPT catalyst system, shown in Figure 3.

The evidence above rules out a free radical initiated autoxidation mechanism. The unreactivity observed when peracetic acid is

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substituted for ethanol suggests peracids are not involved in the oxidation. Although at this time a complete reaction mechanism cannot be substantiated, it appears most likely that the products, 2-hexanone and 2-hexanol, result from a common intermediate. This suggests the metal ion catalyzed decomposition of a hydroperoxide intermediate. The common source of these two products may be RC-(OOH)HCH$_3$.

Acknowledgment. We acknowledge the support of this research by the National Science Foundation and the Office of Naval Research.

Registry No. CoSalMDPT, 15391-24-9; RhCl(PPh$_3$)$_3$, 14694-95-2; 1-hexene, 592-41-6; 2-hexanone, 591-78-6; 2-hexanol, 626-93-7.

Ablative Photodecomposition: Action of Far-Ultraviolet (193 nm) Laser Radiation on Poly(ethylene terephthalate) Films

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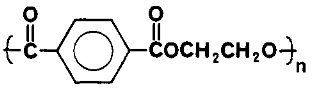
Received August 9, 1982

Several reports[1-6] have been published on the action of far-ultraviolet radiation (193 nm) at laser intensities on small organic molecules. All of these studies were conducted in the gas phase and showed a predominance of two-photon photochemical processes. It is possible to use the 193-nm laser source to obtain controlled one-photon transformations of a small molecule such as 2-, or 3-norcarene in dilute solutions.[7,8] In this communication, it is shown that 193-nm laser radiation leads to novel photochemical transformations in films of poly(ethylene terephthalate) (**1**, hereafter PET). Films of PET of 250 or 75 μm that were free from either a plasticizer or a UV stabilizer were obtained commercially and used as obtained. The $\bar{M}_r$ was $\sim$20 000. The excimer laser (Lambda Physik EMG500) put out pulses of 12-ns duration with intensities in the range 10–180 mJ/cm^2. A repetition rate of 1 Hz or less was used. Films of PET were exposed to the radiation in an evacuated cell through a Spurasil window. The beam was not focused on the film in order to minimize heating effects.



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Single pulses of 193-nm radiation caused the etching of the surface of PET[9] and resulted in numerous gaseous products.[10] Apart from gases such as CO, CO$_2$, and hydrogen (which were not quantitatively analyzed) there were about 30 compounds which ranged from C$_2$ to C$_{12}$.[11] The most important of the latter set was benzene, which was formed with a maximum quantum yield of 0.02. Toluene and benzaldehyde were also identified in yields that amounted to 1/10th of that of benzene, while ethylbenzene was formed in 1/100th of the yield of benzene. In Figure 1 the yield of benzene is plotted as a function of the intensity of the radiation. It is seen that benzene is released as a volatile product only above a threshold intensity and rapidly reaches a maximum value. The upper limit to the quantum yield of benzene may represent a balance between its formation from PET and its destruction by two-photon processes, since the mass of material that was removed by photoetching seemed to increase with intensity.

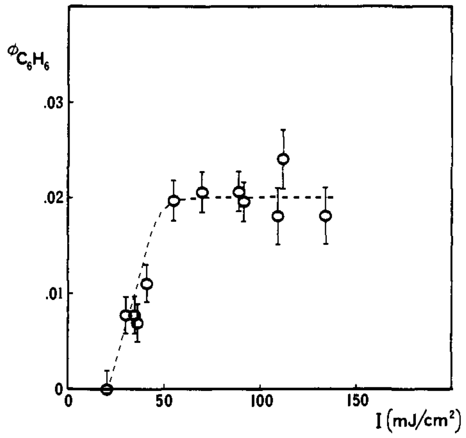

Figure 1. Quantum yield of benzene at various laser pulse intensities (wavelength 193 nm). All determinations are at constant total irradiation intensity. Gas products were *not* exposed to subsequent pulses. Since the pulse width was constant, the abscissa also represents power/cm^2.

The addition of oxygen started to affect the yield of benzene only when 20 torr was present. The quantum yield of benzene was 1/7th of its value in the absence of oxygen even when 200 torr of oxygen was added. The yield of toluene showed a parallel behavior.

It can be calculated that if an extinction coefficient of $\sim 10^4$ L mol^{-1} cm^{-1} is assumed for the monomer unit in PET, the penetration of 193-nm radiation (for 95% absorption) would be only 2700 Å. It can also be expected that the quantum yield for bond break at this wavelength would be of the order of 0.1–1.0, as is usually the case in the far-UV photochemistry of many small organic molecules in the condensed phase at 185 nm.[8] The combination of these two factors would lead to a very high concentration of free radicals in the surface layers of the PET film shortly after a pulse of light is absorbed. The ejection of the photoproducts would result from the large free volume that the small fragments would occupy relative to the polymer chain from which they were derived. The reverse of this phenomenon is well-known from studies on the effect of pressure on polymerization reactions.[12] More recently, McBride and his co-workers[13] have elegantly demonstrated the orientational changes that follow bond break in single crystals of aromatic peresters on photolysis at low temperature. The fragments ejected from the PET film probably carry away the excess energy of the photon pulse, which would be the reason the photoetched film indicates no significant rise in its temperature. The process can therefore be termed an "ablation".[14]

The most surprising result from this study is the nature of the abstraction and recombination reactions that must occur in the PET film in order to give rise to products such as benzene, toluene,

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(1) Jackson, W. M.; Halpern, J. B.; Lin, C.-S. *Chem. Phys. Lett.* **1978**, *55*, 254.

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(9) Scanning electron microphotographs show that the etching is completely and precisely defined by the path of the light beam. There was no indication that the temperature of the film had been raised to a point where it underwent flow.

(10) Products were collected continuously during irradiation by pumping through a U-trap cooled in liquid nitrogen. Analyses were carried out on a Hewlett-Packard GC–mass spectrometer. Benzene, toluene, benzaldehyde, and ethylbenzene were identified by their mass spectra and their retention times.

(11) The intense fluorescence of one or more of the volatile components of the products when excited by 193-nm light was evident even visually in those experiments in which the products were allowed to accumulate in the cell.

(12) Weale, K. E. *Q. Rev. Chem. Soc.* **1962**, *16*, 267.

(13) Walter, D. W., McBride, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 7069, 7074 and earlier references therein.

(14) "To ablate" (verb transitive) is defined by Webster's Collegiate Dictionary (G. C. Merriam: Springfield, 1981) as "to remove by cutting, erosion, melting, evaporation, or vaporization".

0002-7863/82/1504-6784$01.25/0