J. Am. Chem. Soc. **1980**, *102*, 7597-7598

Changeover from Rate-Determining Electron Transfer to Rate-Determining Proton Transfer in the Oxidation of Alkyl Aromatic Compounds by Ceric Ammonium Nitrate[1]

Sir:

The problem of the mechanism of side-chain oxidation of alkyl aromatic compounds by one-electron oxidants (Co^{III}, Mn^{III}, Ce^{IV}, etc.) appears far from being settled.[2] Serious doubts have been raised concerning the hitherto accepted radical cation mechanism (Scheme I).

Scheme I

$$ArCH_3 + M^{n+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCH_3^{+}\cdot + M^{(n-1)+} \qquad (1)$$

$$ArCH_3^{+}\cdot \xrightarrow{k_2} ArCH_2\cdot + H^+ \qquad (2)$$

$$ArCH_2\cdot + M^{n+} \rightarrow \text{products} + M^{(n-1)+} \qquad (3)$$

We have determined the deuterium kinetic isotope effect in the side-chain oxidations of some alkyl aromatic compounds with ceric ammonium nitrate (CAN);[3] the results fully confirm the mechanism of the scheme for the reactions of this metal and also show that the slow step of the reaction can change depending on the substrate structure.

The reactions of CAN with 1,2,3-trimethyl-5-*tert*-butylbenzene (**1**), 1,3-dimethyl-2-(trideuteriomethyl)-5-*tert*-butylbenzene (**1d**), hexamethylbenzene (**2**), perdeuteriohexamethylbenzene (**2d**), *p*-methoxytoluene (**3**), and *p*-methoxytoluene-α,α,α-d_3 (**3d**) have been studied in acetic acid at 25 °C. In all cases only side-chain-substituted products (acetates and nitrates) have been obtained (comparison with authentic specimen). Side-chain attack at the 2-position accounted for 92 ± 1% and 79 ± 1% of the reaction with **1** and **1d**, respectively (VPC analysis). The kinetics have been carried out by following the disappearance of CAN spectrophotometrically at 400 nm. The second-order rate constants (k) have been calculated[5] from time necessary to reach 5% of Ce(IV) consumption, measured at the same CAN concentration and using an excess of substrate. The values are reported in Table I, together with those of the deuterium kinetic isotope effect k_H/k_D. The dependence of k and k_H/k_D upon the Ce(III) concentration is illustrated by the plots in Figure 1.

Table I. Second-Order Rate Constants (k) and Deuterium Kinetic Isotope Effects (k_H/k_D) for Ce(IV)[a] Oxidations of Some Alkylaromatic Compounds in Acetic Acid at 25.0 °C

substrate	[Ce(III)],[b] M × 10^3	k_H,[c] s^{-1} M^{-1}	k_D,[c] s^{-1} M^{-1}	k_H/k_D[d]
1-1d		4.3×10^{-4}	4.3×10^{-4}	1.0
	1.07	6.0×10^{-4}	4.9×10^{-4}	1.2
	2.62	9.3×10^{-4}	7.6×10^{-4}	1.2
2-2d		1.83	1.16	1.6
	0.315	1.77	0.63	2.8
	1.07	1.65	0.33	5.0
	2.62	1.31	0.24	5.4
3-3d		4.7×10^{-1}	1.34×10^{-1}	3.5
	0.317	1.28×10^{-1}	2.4×10^{-2}	5.3
	1.04	7.1×10^{-2}	1.22×10^{-2}	5.8
	2.64	5.8×10^{-2}	9.4×10^{-3}	6.2

[a] $[Ce(IV)]_0 = 1.05 \times 10^{-3}$ M. [b] Concentration of added Ce(III), as $Ce(NO_3)_3 \cdot 6H_2O$. [c] The average error is ±5-7%. [d] The average error is ±10%.

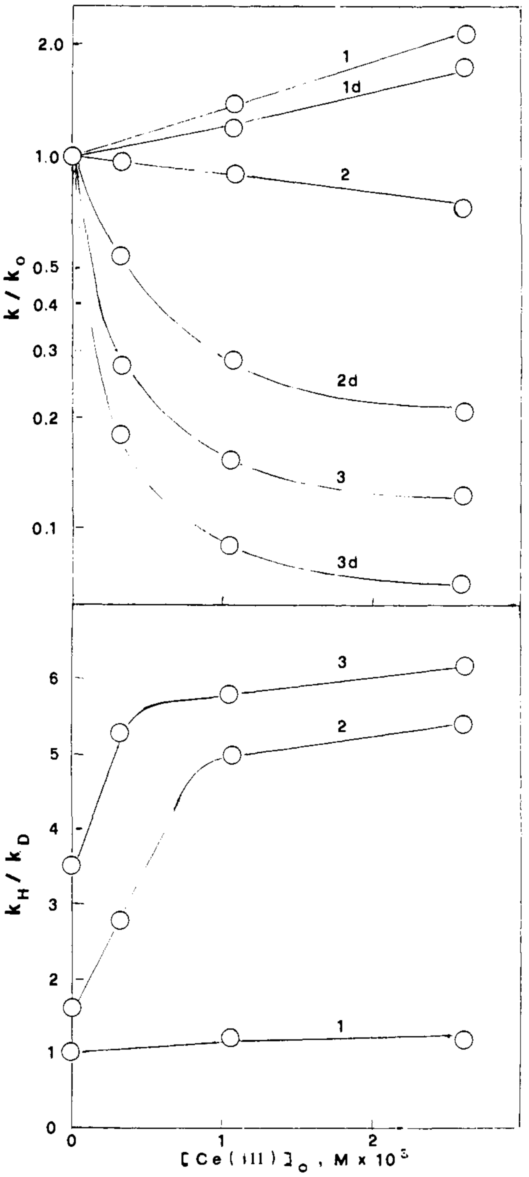

Figure 1. Dependence of k/k_0 (k_0 is the rate constant in the absence of added Ce(III)) and k_H/k_D upon the concentration of added Ce(III) for the substrates investigated (see text). To include all the k/k_0 data investigated in the same plot a logarithmic scale has been used.

The reactions investigated exhibit markedly different behavior. With **1**, no deuterium kinetic isotope effect is observed; both k_H and k_D increase by increasing the concentration of added Ce(III) (probably a salt effect[7]), but k_H/k_D values are hardly affected by the addition of Ce(III). In contrast, k_H/k_D values larger than 1 are found in the reactions of **2** and **3**. In both cases the rate constants decrease and k_H/k_D values increase by increasing the concentration of added Ce(III). The real retarding effect of Ce(III) is probably greater than that actually observed, owing

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(1) Part 7 of the series "Oxidation of Aromatic Compounds by Metal Ions". Part 6: Baciocchi, E.; Mandolini, L.; Rol, C. *J. Org. Chem.* **1980**, *45*, 3906.

(2) (a) Hanotier, J.; Hanotier-Bridoux, M. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1035. (b) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 6830. (c) Eberson, L.; Jönsson, L.; Wistrand, L. G. *Acta Chem. Scand., Ser. B* **1978**, *32*, 520. (d) Baciocchi, E.; Mandolini, L.; Rol, C. *Tetrahedron Lett.* **1976**, 3343.

(3) A k_H/k_D value of 1.8 has been reported for the oxidation of toluene with Ce(IV).[4] However the experimental details of this work are not known. Moreover, toluene has a high oxidation potential and could react by a different mechanism than that of polyalkylbenzenes.

(4) Young, L. B. "Abstracts of Papers", 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; American Chemical Society: Washington, DC, 1976; ORGN-69.

(5) Kinetics of oxidations by Ce(IV) in acetic acid are quite complex, exhibiting a change in the kinetic order of Ce(IV) when CAN concentration is changed. Thus when an excess of aromatic is used, pseudo-first-order kinetics are obtained only during the early stages of the reaction.[2d] Recent work[6] has shown that the phenomenon has to be attributed to salt effects and that the reaction is really first order in Ce(IV).

(6) Okamoto, K.; Takenchi, K.; Murai, O.; Fujü, Y. *J. Chem. Soc., Perkin Trans. 2* **1979**, 490.

(7) It has been clearly shown that the rate of Ce(IV) oxidations is also significantly enhanced by the addition of $LiNO_3$[6] and NH_4NO_3.[2d,8] However, whether these are real medium effects or more specific effects is unknown.

(8) Baciocchi, E.; Mei, S.; Rol, C.; Mandolini, L. *J. Org. Chem.* **1978**, *43*, 2919.

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to the positive salt effect of $Ce(NO_3)_3$.

Clearly, no breaking of the methyl C–H bond takes place in the rate-determining step of the oxidation of **1**. This unequivocally shows that the electron and the proton are lost in subsequent steps, in agreement with the mechanism reported in Scheme I. The formation of the radical cation occurs in the slow step of the reaction as also shown by the observation that the addition of Ce(III) does not retard the rate nor significantly change the k_H/k_D value. Further support for this mechanism comes from the observation that whereas the rate is unaffected by isotopic substitution, the product composition is different for **1** and **1d**, a smaller amount of side-chain substitution at the 2-position being observed with the latter substrate. Accordingly, product composition is determined in the second step which *must* exhibit a kinetic deuterium isotope effect.

The formation of a radical cation from **2** and **3** is easier than from **1**, owing to the lower ionization potential of the former substrates. It also follows that the reactions of **2** and **3** should occur by the radical cation mechanism, the presence of a deuterium kinetic isotope effect and a rate-retarding effect of Ce(III) being determined by a contribution of the rate of the proton abstraction step (eq 2) to the reaction rate.[9] That is, we suggest that, as we go from **1** to **3**, we pass from a situation where $k_2 \gg k_{-1}[\mathrm{Ce(III)}]$ to a situation where $k_2 \lesssim k_{-1}[\mathrm{Ce(III)}]$. With **1**, the condition $k_2 \gg k_{-1}[\mathrm{Ce(III)}]$ clearly holds in all the investigated range of added Ce(III) concentrations. With both **2** and **3**, we are instead in a situation where $k_{-1}[\mathrm{Ce(III)}]$ and k_2 are of comparable magnitude, and consequently by increasing [Ce(III)], an increase in k_H/k_D is observed, especially with **2**. Very likely the changeover of the rate-determining step takes place on going from **2** to **2d**. With the former only a little contribution of the proton-transfer step to the rate is indicated by the small retarding effect of Ce(III); with **2d** such a contribution instead becomes significant (in this case k_2 is smaller than with **2** since hydrogen has been replaced by deuterium) and the rate is strongly slowed down by Ce(III).

On the basis of the above considerations (also supported by the values of k_H/k_D in the absence of added Ce(III)), it would seem that the k_2/k_{-1} ratio decreases in the order **1** > **2** > **3**. Probably, this is mainly due to a decrease, in the same order, of the rate of proton-transfer process. Accordingly, a k_2 value smaller for $\mathbf{2}^{+\cdot}$ than for $\mathbf{1}^{+\cdot}$ is in agreement with the finding that the rate of proton transfer from a polymethylbenzene radical cation decreases with the increase in the number of methyl groups.[2c,12] It is also likely that k_2 decreases on going from $\mathbf{2}^{+\cdot}$ to $\mathbf{3}^{+\cdot}$, since the difference in the capacity of stabilizing a radical cation and a benzylic free radical should be much greater for a methoxy than for a methyl group. Thus, the conversion into the free radical should be energetically more costly for $\mathbf{3}^{+\cdot}$ than for $\mathbf{2}^{+\cdot}$.

Finally, it appears that in these reactions there can be such a delicate balance between $k_{-1}[\mathrm{Ce(III)}]$ and k_2 that even subtle changes of the substrate structure can change the slow step of the reaction. Thus, in the study of these oxidations, the determination of the deuterium kinetic isotope effect for a *single* substrate can be of limited significance for drawing general conclusions.

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(9) The possibility of a secondary deuterium kinetic isotope effect should be considered. Actually, the reversible oxidation potential of **2d** has been found about 5 mV lower than that of **2**, and this difference allows us to calculate a secondary deuterium kinetic isotope effect of about 1.2 for the formation of $\mathbf{2}^{+\cdot}$ from **2**. On this basis even lower, and, therefore, negligible values of secondary k_H/k_D should be predicted for the reactions involving **1** and **3**, since in these cases only a CH_3 group has been replaced by a CD_3 group. Significantly larger secondary k_H/k_D (up to ~2) should be, in contrast, possible on the basis of a recent study of charge-transfer complexes of alkyl aromatic compounds.[10] However this prediction seems somewhat in contrast with the finding that K_D/K_H is ~1.1 (an inverse isotope effect!) for the association of *p*-xylene and toluene with fluoranil.[11]

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(11) Chudek, J. A.; Foster, R. *Tetrahedron* **1978**, *34*, 2209.

(12) Sehested, K.; Holcman, J. *J. Phys. Chem.* **1978**, *82*, 651.

Polyoxoanion Supported Metal Carbonyls: Syntheses of the $[(OC)_3M(Nb_2W_4O_{19})]^{3-}$ Anions (M = Rhenium and Manganese)

Sir:

The reaction between d^6 metal carbonyl complexes and metal oxide surfaces yields surface-bound species whose chemical and physical properties have been examined extensively.[1] The variety of behaviors displayed by these species has led us to undertake a systematic study of metal carbonyl units bound to the oxide surfaces of polyoxoanion clusters. In this communication, we report the synthesis and characterization of the first adducts of this type, the $[(OC)_3Re(Nb_2W_4O_{19})]^{3-}$ anion and its manganese analogue, containing metal tricarbonyl units bonded to a triangle of oxygen atoms on the surface of the $Nb_2W_4O_{19}{}^{4-}$ anion.

Refluxing a solution of $[(n\text{-}C_4H_9)_4N]_4(Nb_2W_4O_{19})$ (**1**),[2] prepared from aqueous $Na_2[(CH_3)_4N]_2(Nb_2W_4O_{19})$[4] by using a cation-exchange resin, and an equimolar amount of $[(OC_3)Re(NCCH_3)_3](PF_6)$[5] for 2 h in CH_3CN under N_2 followed by cooling to −30 °C yields a pale yellow crystalline product formulated as $[(n\text{-}C_4H_9)_4N]_3[(OC)_3Re(Nb_2W_4O_{19})]$ (**2**)[6a] after recrystallization from $CH_3CN/CH_3C_6H_5$ by slow evaporation. The IR spectrum of **2**[6b] contains (1) two bands in the carbonyl stretching region characteristic of a C_{3v} metal tricarbonyl unit,[7] (2) the same pattern of absorptions in the 850–1000-cm^{-1} terminal oxygen stretching region observed for **1**[2b] displaced to higher energy by 25–40 cm^{-1}, and (3) absorptions in the 700–850-cm^{-1} bridging oxygen region which differ in number, frequency, and shape from those observed for **1** in the same region. If the 18-electron rule is applied to Re, these data favor an anion structure for **2** in which a $(OC)_3Re^+$ unit is bonded to a triangle of three contiguous bridging oxygen atoms of the $Nb_2W_4O_{19}{}^{4-}$ anion.[8] They fail, however, to indicate the locations of the Nb and W centers within the $Nb_2W_4O_{19}{}^{4-}$ unit relative to the Re atom. Since X-ray diffraction studies have thus far been plagued by disorder problems,[9] an ^{17}O NMR

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(2) (a) Anal. Calcd for $C_{64}H_{144}N_4Nb_2W_4O_{19}$: C, 35.02; H, 6.61; N, 2.55; Nb, 8.46; W, 33.50. Found: C, 34.95; H, 6.67; N, 2.47; Nb, 8.36; W, 33.62. (b) IR (Nujol, 650–1000 cm^{-1}) 733 (sh, br), 783 (s, br), 880 (s), 892 (s), 927 (s), 950 (m) cm^{-1}. Cf. ref 3.

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(6) (a) Anal. Calcd for $C_{51}H_{108}N_3ReNb_2W_4O_{22}$: C, 27,56; H, 4.90; N, 1.89; Re, 8.38; Nb, 8.36; W, 33.08. Found: C, 27.60; H, 4.97; N, 1.85; Re, 8.21; Nb, 8.60; W, 32.85. (b) IR (Nujol, 700–1000 cm^{-1}) 740 (s), 759 (sh), 810 (s), 826 (sh) [bridging oxygens], 884 (m) [cation], 918 (s), 928 (s), 960 (s), 978 (m) [terminal oxygens] cm^{-1}. IR (CH_3CN, 1850–2050 cm^{-1}) 1897 (s, br), 2020 (s) cm^{-1}.

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(8) This mode of bridging oxygen bonding has been observed in $Mn(Nb_6O_{19})_2{}^{12-}$ and proposed for $(H_2NCH_2CH_2NH_2)(H_2O)M(III)(Nb_6O_{19})^{5-}$, M = Cr, Co: Flynn, C. M.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 178, 335.

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