

HYDROGEN ATOM ABSTRACTION BY TRANSITION METAL COMPLEXES

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ABSTRACT

A key step in many oxidation reactions is hydrogen atom abstraction by a metal-containing reactive site. We have examined oxidations of alkanes and alkylaromatic compounds by metal-oxo compounds and metal coordination complexes, including chromyl chloride (CrO_2Cl_2), permanganate, manganese μ -oxo dimers, copper(III) compounds, and iron(II)-diimine complexes. The data indicate that many of the reactions proceed by initial hydrogen atom abstraction to give the hydrocarbyl radical. Addition of $\text{H}\cdot$ to the metal complex occurs with protonation of a ligand and one-electron reduction of the metal center. For example, $\{(\text{phen})_2\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{phen})_2\}^{3+}$ is reduced first to $\{(\text{phen})_2\text{Mn}(\mu\text{-O})(\mu\text{-OH})\text{Mn}(\text{phen})_2\}^{3+}$ with protonation of a bridging oxo group. The rates at which these reagents abstract $\text{H}\cdot$ are quantitatively related to their thermodynamic affinity for $\text{H}\cdot$ (in other words, the strength of the O-H or N-H bond they form). On this basis, there are strong analogies to well-known organic radical chemistry, even though the oxidants may not have any radical character. In efforts toward a more detailed understanding of H-atom transfer, studies are ongoing of hydrogen-atom self exchange rates.

INTRODUCTION

The oxidation of hydrocarbons often involves initial abstraction of a hydrogen atom to form a carbon radical (eq 1). This occurs in combustion reactions and in a range of industrial partial oxidation processes, many of which are done on an enormous scale. Hydrogen atom abstraction is also implicated in a variety of biochemical processes and is increasingly valuable in organic synthesis. The abstracting agent in H-atom transfer reactions is typically a reactive main group radical, a species with at least one unpaired electron spin. For this reason, H-atom transfer is classified as a "radical reaction."



The current understanding of rates of hydrogen abstraction by radicals is based not on radical character but on the enthalpy of reaction.¹ This was first enunciated by Evans and Polanyi in the 1930s. The enthalpy change (ΔH) for reaction 1 is simply the difference between the strength of the R-H bond being cleaved and the strength of the H-X bond formed. Activation energies E_a (and rate constants $\log k$) correlate closely with ΔH when comparing similar radicals. This is reminiscent of the Marcus-Hush theory of electron transfer, in which rates correlate with driving force as long as reagents of similar intrinsic barriers are compared. Different classes of radicals fall on different correlation lines. The standard explanation for this is termed polar effects, a result of the overlap of the half-occupied frontier orbital of the radical with the HOMO and LUMO of the C-H bond.

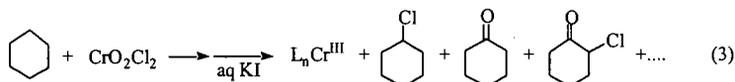
We have been exploring hydrocarbon oxidations by transition metal complexes, many of which proceed by $\text{H}\cdot$ transfer to a ligand on the transition metal (eq 2). The presence or absence



of unpaired electrons in such complexes does not correlate with reactivity and therefore cannot be used to understand $\text{H}\cdot$ transfer. So instead of looking at the spin state of the metal complex $\text{M}(\text{X})\text{L}_n$, it has often been assumed that there is a requirement for radical character at the ligand that accepts the H (X in eq 2). We find that the metal reactions are predominantly influenced by the ground state thermodynamics (the ΔH) rather than by radical character. Similar conclusions have recently been reached for hydrogen atom transfer between alkanes and alkenes (and related reactions).² We are now beginning to explore what is meant by the phrase *similar radicals* when the abstractor is not a radical. [An experimental section is not included here; the reader is referred to the original, peer-reviewed literature for such information.^{5,7,8}]

RESULTS AND DISCUSSION

The oxidation of alkanes by chromyl chloride, CrO_2Cl_2 (e.g., eq 3), is known as the Étard reaction and dates from the nineteenth century. In the 1960s, Wiberg and co-workers argued convincingly for organic radical intermediates (though other mechanisms have been discussed).³ Organic radicals have also been implicated in the oxidations of alkylaromatic compounds by permanganate.⁴ Detailed mechanistic studies in our labs⁵ have indicated that both types of reactions occur by initial hydrogen atom transfer (e.g., eq 4).



Hydrogen atom abstraction by CrO_2Cl_2 and permanganate was at first surprising because these are d^0 , closed-shell species, with no unpaired spin density. Their reactions are better explained on the basis of the strength of the bond they can make to $\text{H}\cdot$, which can be calculated by a thermochemical cycle (Scheme 1).^{5,6} For permanganate, the value derived is 80 kcal/mol. As shown in Figure 1, the rate constant for hydrogen abstraction from toluene for permanganate is close to what would be predicted based on the Polanyi correlation of rates with driving force.

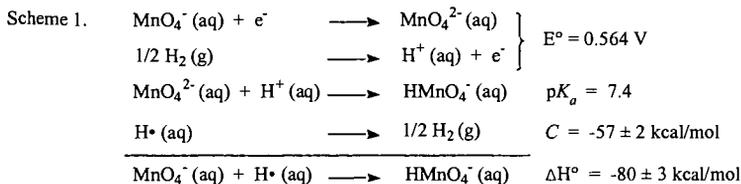
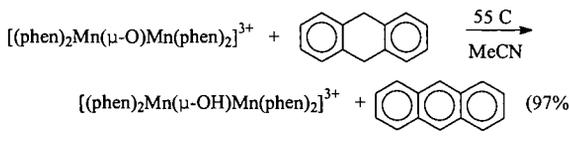
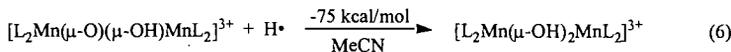
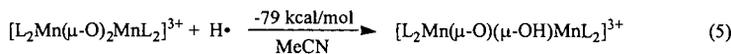


Figure 1 $\log k$ vs. O-H bond strength for reactions of toluene with ${}^n\text{Bu}_4\text{NMnO}_4$ and $\text{RO}\cdot$.

In principle, any active site with affinity for $\text{H}\cdot$ (that is, an affinity for both an electron and a proton) should be able to abstract hydrogen atoms from a substrate. And the rate constant for H-atom transfer should be roughly predictable from the Polanyi correlation illustrated in Figure 1. Our first efforts in this direction involved the dimanganese di- μ -oxo complex $[\text{Mn}_2(\mu\text{-O})_2(\text{phen})_4]^{3+}$.⁷ Redox potential and pK_a measurements yielded the O-H bond strengths in eqs 5 and 6 (using a variant of Scheme 1). As predicted from this bond strength, $[\text{Mn}_2(\mu\text{-O})_2(\text{phen})_4]^{3+}$ oxidizes dihydroanthracene (DHA) to anthracene in high yield over 11 h at 55 °C (eq 7; traces of anthrone and anthraquinone are also formed). Kinetic and mechanistic studies⁷ indicate a pathway of initial hydrogen atom abstraction from the weak C-H bond, with a deuterium isotope effect $k_{\text{DHA}}/k_{d_{12}\text{-DHA}}$ of 4.2 ± 0.3 at 55 °C and formation of bifluorenyl and 9-fluorenone from fluorene.



Hydrogen atom abstraction has also been observed for an iron(III) complex,⁸ as shown in equation 8. Complex 1 has an affinity for an electron, because the Fe³⁺ center is oxidizing, and an affinity for a proton, because one of the biimidazole ligands is deprotonated. The measured *E* and p*K_a* values translate into an affinity for H• of 76 ± 2 kcal/mol. H-atom abstraction reactivity is perhaps surprising in this case because the proton accepting site is three bonds removed from the redox active iron.

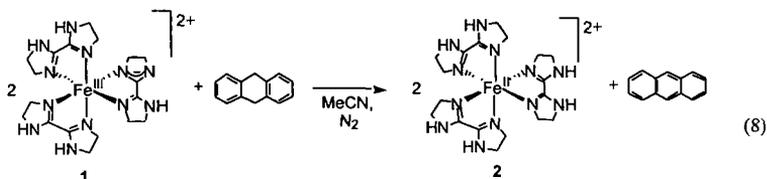


Figure 2 plots the rate constants for hydrogen abstraction from DHA versus the strength of the O-H or N-H bond formed for oxygen radicals, permanganate, the manganese μ -oxo dimers, and the iron complex 1. Remarkably, the rate constants for the metal complexes are within a factor of 10² of the values predicted by linear extrapolation of the values for ^tBuO• and ^{sec}BuOO• (Figure 2). This is a one-parameter fit of the rate constants, based only on the ground state affinity of the oxidant for H•. While it is not yet known how general a result this will be, it seems clear that analyzing a hydrogen transfer reaction should start with the relevant bond strengths.

Figure 2. log*k* vs. X-H bond strength for H-atom abstraction from dihydroanthracene.

Viewed from another perspective, the rough success of the correlation in Figure 2 indicates that ^tBuO•, ^{sec}BuO₂•, and the four metal complexes behave as “similar radicals.” We are now trying to understand what makes these oxidants are similar. A frontier orbital/polar effect argument is difficult to make, as the orbital patterns of the metal complexes are varied and quite different from that of the oxygen radicals. A polar effect rationale would also incorrectly predict that the iron complex would not correlate with the others, because it has a nitrogen rather than an oxygen as the atom that receives the hydrogen. An alternative possibility, following Marcus theory, is that these reagents are similar because they have similar intrinsic barriers. To explore this view, we have been studying the possible hydrogen atom self-exchange reaction between iron complexes 1 and 2. The oral presentation will describe recent results, and discuss the possibility that intrinsic barriers and polar effects are both needed to understand H-atom transfer reactions.

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