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Lewis-acid Catalysed Oxidation of Alkanes by Chromate and Permanganate

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The oxidation of alkanes by chromate and permanganate has been found to be greatly accelerated by Lewis acids such as BF_3 and $AlCl_3$; reaction occurs within minutes at room temperature in the presence of just a few equivalents of the Lewis acids.

Chromate and permanganate have long been used as oxidants for a variety of organic functional groups.[1] Their use in the oxidation of alkanes is, however, limited; refluxing conditions are often required to oxidize unactivated C–H bonds. Bronsted acids are often added to increase the rate of reaction; however, the use of Lewis acids to enhance the reactivity of these traditional oxidants has not been reported. We have reported recently that the oxidation of alkanes by an oxoruthenium species is accelerated by Lewis acids.[2] Some evidence can be found in the literature which suggests that Lewis acids may also interact with chromate and permanganate. For example, $Zn(MnO_4)_2$ and $Ba(MnO_4)_2$ are more reactive toward the oxidation of organic substrates than is $KMnO_4$;[3] chromate is known to form complexes with metal ions, *e.g.* Fe^{3+}, which are usually rather unstable.[4] We report here a study of the effects of Lewis acids on the oxidation of alkanes by chromate and permanganate; our results indicate that huge accelerating effects are observed upon addition of only a few equivalents of Lewis acids.

Upon adding a few equivalents of $BF_3 \cdot MeCO_2H$ to a solution of $[NBu^n_4]_2[Cr_2O_7]$ in CH_2Cl_2 containing cyclohexane at room temperature the initially orange solution turned purple within minutes. Analysis by GC and GC–mass spectrometry indicated the presence of cyclohexanone. The reaction was further enhanced by the addition of a small amount of acetic anhydride.† Performing the reaction in MeCN lowered the yield. Only a trace amount of product was detected after 17 h in the absence of BF_3. Other Lewis acids such as $AlCl_3$, $FeCl_3$ and $Cu(O_3SCF_3)_2$ gave similar yields but the rates were slower, while $ZnCl_2$ and AgO_3SCF_3 were rather ineffective. Representative results are shown in Table 1. Similar accelerating effects were also observed with other oxochromium(VI) species. Thus, under similar conditions, 16% of cyclohexanone was produced from BF_3 and chromyl acetate. In the case of $[C_5H_5NH][CrClO_3]$ the products contained 15% cyclohexanone and 7% cyclohexyl chloride. Results for BF_3-catalysed oxidation of other alkanes and aromatic hydrocarbons by dichromate are shown in Table 2. In all cases carbonyl products were formed exclusively from primary and secondary C–H bonds. With adamantane, oxidation occurred only at the tertiary C–H bonds, presumably to produce initially adamantan-1-ol which then reacted with acetic anhydride to produce adamantan-1-yl acetate. The BF_3-catalysed oxidation of cyclohexane has a kinetic isotope effect (k_H/k_D) of 3.9, while values of 3.1 and 6.4 were found for the oxidation of

Table 1 Effect of Lewis acids on the oxidation of cyclohexane by $[NBu^n_4]_2[Cr_2O_7]$[a]

Lewis acid	Solvent (volume)	Reaction time	Cyclohexanone[b] (% yield)
$BF_3 \cdot MeCO_2H$	CH_2Cl_2 (5 cm^3)	20 min	26
	CH_2Cl_2 (5 cm^3)–$(MeCO_2)_2O$ (120 µl)	5 min	37
	MeCN (5 cm^3)	5 min	8
None	CH_2Cl_2 (5 cm^3)–$(MeCO_2)_2O$ (120 µl)	17 h	2
$AlCl_3$	CH_2Cl_2 (3 cm^3)–$MeCO_2H$ (1 cm^3)	3 h	31[c]
	MeCN (5 cm^3)–$(MeCO_2)_2O$ (0.5 cm^3)	3 h	29
$Cu(O_3SCF_3)_2$	CH_2Cl_2 (3.5 cm^3)–$MeCO_2H$ (0.5 cm^3)	3 h	37
$FeCl_3$	CH_2Cl_2 (3 cm^3)–$MeCO_2H$ (1 cm^3)	5 h	25[d]
$ZnCl_2$	CH_2Cl_2 (3 cm^3)–$MeCO_2H$ (1 cm^3)	4 h	6

[a] 23 °C, 0.08 mmol $[NBu^n_4]_2[Cr_2O_7]$, 0.4 mmol Lewis acid, 1 cm^3 cyclohexane. [b] 100 × mol of product/mol of oxidant. [c] Cyclohexanol was also produced in 15% yield. [d] 2% Cyclohexyl chloride was also detected.

Table 2 Oxidation of organic substrates by $[NBu^n_4]_2[Cr_2O_7]$ catalysed by BF_3[a]

Substrate	Product (% yield)[b]
Cyclohexane	Cyclohexanone (37)
Cyclooctane	Cyclooctanone (23)
Pentane	Pentan-2-one (29), -3-one (13)
Hexane	Hexan-2-one (21), -3-one (16)
Heptane	Heptan-2-one (19), -3-one (13), -4-one (9)
Adamantane[c]	Adamantan-1-yl acetate (67)
Toluene	Benzaldehyde (55)
Ethylbenzene	Acetophenone (75)

[a] 23 °C, 5 min, 0.08 mmol $[NBu^n_4]_2[Cr_2O_7]$, 0.4 mmol $BF_3 \cdot MeCO_2H$, 5 cm^3 CH_2Cl_2, 120 µl acetic anhydride, 1 cm^3 cyclohexane. [b] 100 × mol of product/mol of oxidant. [c] 40 mg were used.

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† This produced a homogeneous solution which was otherwise slightly turbid.

Table 3 Effect of Lewis acids on cyclohexane oxidation by $KMnO_4$ in acetonitrile *

Lewis acid	*t*	Product (% yield)	
		Cyclohexanone	Cyclohexyl chloride
$BF_3 \cdot MeCO_2H$	5 min	42	—
$AlCl_3$	30 min	15	35
$FeCl_3$	1 h	8	12
$ZnCl_2$	1 h	8	—
$Cu(O_3SCF_3)_2$	2 h	4	—
None	17 h	—	—

* 0.04 mmol $KMnO_4$, 0.16 mmol Lewis acid, 2.25 cm^3 MeCN, 0.25 cm^3 cyclohexane.

Table 4 Oxidation of organic substrates by $KMnO_4$ in acetonitrile catalysed by BF_3[a]

Substrate	Product (% yield)
Cyclohexane	Cyclohexanone (42)
Cyclooctane	Cyclooctanone (55)
Hexane	Hexan-2-one (18), -3- one (14)
Adamantane[b]	Adamantan-1-ol (31), -2-ol (5), 1,2,3,5,6,7-hexahydro-2,6-methanoinden-4-one (24)
Toluene	Benzaldehyde

[a] 23 °C, 10 min, 0.04 mmol $KMnO_4$, 0.32 mmol $BF_3 \cdot MeCO_2H$, 0.25 cm^3 substrate, 2.25 cm^3 MeCN. [b] 50 mg were used.

3-ethylpentane and diphenylmethane respectively by chromic acid in 91% acetic acid.[5]

Dramatic accelerating effects by Lewis acids were also observed in the oxidation of alkanes by $KMnO_4$. Thus, the purple colour of a solution of $KMnO_4$ and cyclohexane in MeCN was discharged within a couple of minutes at room temperature upon adding a few equivalents of $BF_3 \cdot MeCO_2H$, with concomitant production of cyclohexanone. In the absence of BF_3 no colour change and no products were observed after 24 h. Other Lewis acids such as $AlCl_3$, $FeCl_3$, $ZnCl_2$ and $Cu(O_3SCF_3)_2$ were less effective (Table 3). In the case of $AlCl_3$ and $FeCl_3$ the major product was cyclohexyl chloride. Results for the oxidation of other alkanes and aromatic hydrocarbons are shown in Table 4. The BF_3-catalysed oxidation of cyclohexane has a kinetic isotope effect of 4.1, which is similar to the value of 4.3 obtained in the trifluoroacetic acid-catalysed oxidation.[6]

The similarities in product distributions (ketones are formed predominantly over alcohols) and kinetic isotope effects between reactions catalysed by Lewis acids and by protons suggest that the mechanisms are similar in the two cases. The Lewis acid (E) most likely acts by bonding to an oxo ligand: $M = O + E \longrightarrow M = O \rightarrow E$. The accelerating effects are thus due to electron withdrawal by the Lewis acid, which would make the oxometal complex more strongly oxidizing. A mechanism involving other reactive species such as $OH^{\bullet}$ radical can be ruled out since the observed kinetic isotope effects are much larger than those for $OH^{\bullet}$ (1.1 for cyclohexane).[7] Attempts to isolate Lewis-acid adducts of dichromate and permanganate have so far been unsuccessful owing to their instability. However, adducts of less-oxidizing oxometal species with weak Lewis acids have been isolated. For example, the complexes $[(ReMe_4O)_2Mg(thf)_4]$ and $[\{Re(CH_2SiMe_3)_4O\}_2Mg(thf)_2]$ (thf = tetrahydrofuran) have been prepared and their crystal structures indicate bonding of the oxide ligands to Mg^{2+}.[8] It is noteworthy that the accelerating effects of Lewis acids such as BF_3 and $AlCl_3$ seems to be much greater than that of Bronsted acids. The higher reactivity of $Zn(MnO_4)_2$ and $Mg(MnO_4)_2$ compared with $KMnO_4$ is likely due to the higher Lewis acidity of the dications.

In conclusion, oxidation by chromate and permanganate readily occurs at room temperature in the presence of just a few equivalents of Lewis acids. This finding should increase the scope of applications of these common oxidants.

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