A Novel Oxidizing Reagent Based on Potassium Ferrate(VI)[1]

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A new, efficient preparation has been devised for potassium ferrate(VI) (K_2FeO_4). The ability of this high-valent iron salt for oxidizing organic substrates in nonaqueous media was studied. Using benzyl alcohol as a model, the catalytic activity of a wide range of microporous adsorbents was ascertained. Among numerous solid supports of the aluminosilicate type, the K10 montmorillonite clay was found to be best at achieving quantitative formation of benzaldehyde, without any overoxidation to benzoic acid. The roles of the various parameters (reaction time and temperature, nature of the solvent, method of preparation of the solid reagent) were investigated. The evidence points to a polar reaction mechanism. The ensuing procedure was applied successfully, at room temperature, to oxidation of a series of alcohols to aldehydes and ketones, to oxidative coupling of thiols to disulfides, and to oxidation of nitrogen derivatives. At 75 °C, the reagent has the capability of oxidizing both activated and nonactivated hydrocarbons. Toluene is turned into benzyl alcohol (and benzaldehyde). Cycloalkanes are also oxidized, in significant (30−40%) yields, to the respective cycloalkanols (and cycloalkanones). Thus, potassium ferrate, used in conjunction with an appropriate heterogeneous catalyst, is a strong and environmentally friendly oxidant.

Introduction

For oxidation of organic functionalities, one turns often to high-valent metal oxides or their mineral salts. Classic reagents of this type are manganese dioxide (MnO_2), potassium permanganate ($KMnO_4$), chromium trioxide (CrO_3), potassium chromate (K_2CrO_4), and potassium dichromate ($K_2Cr_2O_7$).[2] These are all frequently-used reagents, whether in the laboratory or in industry, and yet they are beset with multiple liability. For satisfactory and reproducible results, these oxidants demand rigorous control of the experimental conditions. In particular, their mode of preparation and the detailed nature of the activation process, in preparation for their use, has considerable influence on the practical results. For instance, with manganese dioxide, marked variations in activity occur, depending on the method used to form and then to treat the oxide precipitate.[3]

Another drawback against such oxidants and their use in multistage organic synthesis, in spite of their power, is their lack of selectivity. For instance, overoxidation of aldehydes to carboxylic acids and the degradation of unsaturated substrates are often unavoidable side reactions. Furthermore, the elevated reflux temperatures required by some oxidation procedures will favor inopportune secondary reactions. Likewise, the presence of strong acids or bases, which are required adjuncts as catalysts for some reactions, often leads to detrimental side reactions. As an example, the oxidation of primary alcohols to aldehydes by a chromium(VI) salt in sulfuric acid is often accompanied by formation of an hemiacetal between the resulting aldehyde and the alcohol substrate, followed by the ready oxidation of this intermediate to an ester.[4]

In addition to their lack of selectivity and their difficulty in activating, oxidants based on chromium[5] and on manganese[6] are corrosive, and they are irritants for the skin and for sensitive body parts such as the eyes. They are violently toxic to man and to the environment. Derivatives of chromium(VI) in particular are well-known carcinogens.[7] In view of the ever more compelling environmental constraints, it has become unacceptable for industrial effluents and wastes to contain such highly toxic transition metals. Design of new, less polluting oxidation procedures has become a priority for the chemical industry.[8] A recent case at hand is that of the K3 vitamin. This molecule, menadione, useful for human medicine, too, is used in vast amounts as a complement to animal feed. For its preparation, 2-methylnaphthalene is oxidized to a 1,4-quinone. The present industrial process requires a mixture of chromic and sulfuric acids for this key step. It generates no less than 18 kg of chromium waste per kilogram of K3 vitamin product. A new catalytic oxidation procedure was patented and published quite recently.[9] Hydrogen peroxide oxidizes 2-methylnaphthalene in the presence of methyltrioxorhenium (H_3CReO_3) as the catalyst. This has the advantage of a marked reduction in the volume and toxicity of the spent reagents.

Our approach to clean and selective oxidations is to make use of potassium ferrate(VI) as the oxidant in

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combination with an aluminosilicate solid. Association of a ferric salt with a clay support had been pioneered in this laboratory in the 1980s, leading to the design of the "clayfen" supported reagent,[10] with numerous uses in organic synthesis,[11] including the mild and selective oxidation of alcohols to carbonyl derivatives.[12] We reasoned that replacing iron(III) with iron(VI) should boost the oxidizing ability of the reagent, while the continued presence of a microporous adsorbent of the clay or zeolite type would be conducive to the high selectivities our supported reagents and catalysts have repeatedly shown. By contrast with other transition metals, iron is singled out as being considered nontoxic.[13] In addition, replacement of both Brønsted (H_2SO_4, HNO_3, etc.) and Lewis acids ($AlCl_3$, $TiCl_4$, etc.) with aluminosilicate solids also contributes to decreasing the amount of toxic and corrosive wastes.

Why Potassium Ferrate(VI)?

Potassium ferrate (K_2FeO_4) is the best known member among the family of iron(VI) derivatives. It is made and purified more easily, and it is also used in making other ferrates. A quick survey shows that it is both more stable and more readily made. The ferrates of alkaline earths $SrFeO_4$ or $BaFeO_4$ and their hydrates can be obtained indirectly from reaction between a solution of the acetate or chloride of the metal and potassium ferrate.[14,15] Barium ferrate ($BaFeO_4$), as the monohydrate, can be prepared in like manner by precipitation from an alkaline solution of sodium ferrate upon addition of a saturated solution of barium nitrate.[16] To form the mixed potassium−strontium ferrate ($K_2Sr(FeO_4)_2$), a more complex system consisting of $Sr(OAc)_2$, $Sr(OH)_2$, KCl, KOH, and K_2FeO_4 was used.[17] Such methods lack generality however. Losana described in 1925 the preparation of numerous metallic ferrates by exchange from $BaFeO_4$ or K_2FeO_4.[18] But the truth is that subsequent attempts at preparing calcium or transition metal (Co^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Zn^{2+}) ferrates from K_2FeO_4 have failed.[19,20] The expected products did not precipitate, or, when they did, their instability led them to immediate decomposition and evolution of dioxygen. Only silver ferrate (Ag_2FeO_4) could be obtained from K_2FeO_4 and $AgNO_3$. It is not very stable at ambient temperature, though, and has to be stored in a refrigerator.[21]

Sodium ferrate (Na_2FeO_4) has a behavior different from those of other ferrates and remains soluble in an aqueous solution saturated in sodium hydroxide. Its preparation from an aqueous medium is thus made difficult and leads to rather impure samples. In the absence of solvent, conversely, it is possible to form the Na_4FeO_5 salt by heating to 370 °C a mixture of Fe_2O_3 and Na_2O_2 under an atmosphere of dioxygen. Rigorous control of the experimental conditions is required in order to minimize the amount of iron(III) and iron(IV) derivatives formed as byproducts contaminating the desired Fe(VI) salt.[22,23]

Fortunately, K_2FeO_4 provides a better entry into the group of iron(VI) derivatives. Many preparations of this salt in aqueous solution take advantage of both the stability of the ferrate dianion in basic medium and the insolubility of K_2FeO_4 in a saturated solution of potassium hydroxide. This ensures first formation and second isolation through precipitation of potassium ferrate.

Such a procedure can be transposed to preparation of both rubidium and cesium ferrates (Rb_2FeO_4 and Cs_2FeO_4).[24] The cost of the RbOH and CsOH hydroxides makes impractical any but small-scale preparation of these ferrates.

Preparation of Potassium Ferrate(VI)

The history thread gives meaning to the present procedures. As early as 1702, the German chemist and physician Georg Stahl mentioned the appearance of an unstable purplish red color when the molten mass resulting from detonation of a mixture of saltpeter and iron filings was dissolved in water.[25] When Eckeberg[26] and Becquerel[27] in 1834 heated to red mixtures of potash and various iron ores, they also observed similar colors, which we now know to be diagnostic of the FeO_4^{2-} ferrate dianion. As for attribution of this color to a high-valent iron species indeed, credit goes to Frémy, who in the 1840s suggested a formula of the FeO_3 type.[28] Even though this FeO_3 oxide was never isolated, the presence of hexavalent iron in potassium ferrate and barium ferrate was demonstrated by various methods during the ensuing period, allowing Moeser to write a detailed review of ferrates and their chemistry in 1897.[29]

Moeser described three types of preparation for potassium ferrate: *viz.*, a dry way, heating to red various potassium- and iron-containing minerals; an electrochemical way, electrolyzing a potash solution with an iron anode; and a wet way, oxidizing a basic solution of a Fe(III) salt by an hypochlorite or hypobromite. Among these three approaches, the 20th century has privileged the third and last. Dry reactions imply detonation and elevated temperatures. They are considered dangerous (we agree) and too difficult to implement, and they have become obsolete. The only relatively recent contribution of that nature, by Russian authors, describes preparation of potassium ferrate by calcination of a mixture of ferric oxide and potassium peroxide at 350−370 °C under a dioxygen flow.[22] As for anodic oxidation by an iron electrode dipped in a concentrated solution of an alkaline

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hydroxide, it remains another access to ferrates that has retained only marginal interest. It has benefited from recent improvements though, such as superposition of an alternative current to the direct current for electrolysis: such a time modulation of anodic polarization improves the electrochemical yield.[30]

Hrostowski and Scott described in 1950 preparation of potassium ferrate by the wet method. Their procedure implies prior formation of *sodium* ferrate from solutions of ferric chloride and sodium hypochlorite in the presence of sodium hydroxide. Addition of potassium hydroxide then serves to precipitate potassium ferrate from the sodium solution. Although the purity of the samples from this preparation can be as high as 96.9%, the potassium ferrate yield remains low, no better than 10−15%.[31] Modifying the experimental procedure to combine the preparation and purification steps allowed Thompson *et al.*, without sacrificing the high purity (92−96%), to improve the yield to the 44−76% range. Their protocol[32] and their analysis of the potassium ferrate product by a redox titration[33] remain today the standard methodology for preparing and evaluating the purity of potassium ferrate. However, Williams and Riley contributed a significant improvement, bypassing the intermediate formation of sodium ferrate through use of *potassium* hydroxide and hypochlorite. These authors have also simplified the purification of the precipitate. As a consequence, the preparation of potassium ferrate takes less time, and the yields are raised to better than 75%, but at the cost of some loss in purity, which hovers now in the 80−90% range.[34]

To combine high yields and purities while holding to a simple, straightforward experimental procedure, we have further modified the method of Williams and Riley. Their reaction scheme remains unchanged. A concentrated, strongly alkaline solution of potassium hypochlorite is first generated by bubbling chlorine into cold, aqueous potassium hydroxide (eq 2). The potassium chloride byproduct that precipitates upon addition of an excess of KOH is removed by filtration, and iron(III) nitrate is added to the resulting solution. It is readily oxidized to iron(VI), and the solution turns dark purple as ferrate dianions are formed (eq 3). Solid potassium hydroxide is then added, and potassium ferrate precipitates. It is filtered off and purified as discussed below. When a chlorine cylinder is not available or is better avoided for security reasons, the gas can conveniently be generated by dropping concentrated hydrochloric acid on potassium permanganate in a separate vessel (eq 1).

$$KMnO_4 + 8HCl \rightarrow MnCl_2 + {}^{5}/{}_{2}Cl_2\uparrow + 4H_2O + KCl \quad (1)$$

$$Cl_2 + 2KOH \rightarrow KClO + KCl + H_2O \quad (2)$$

$$2Fe(NO_3)_3 + 3KClO + 10KOH \rightarrow 2K_2FeO_4 + 3KCl + 6KNO_3 + 5H_2O \quad (3)$$

Attempts to use commercial bleach solutions to oxidize the iron(III) salt led to the formation of ferrate anions, but due to their high dilution, the precipitation of K_2FeO_4 was not achieved. Other strong oxidizers available either in pure form (potassium persulfate, $K_2S_2O_8$) or in concentrated solution (30% aqueous hydrogen peroxide) were also investigated as an alternative to concentrated aqueous potassium hypochlorite, but these failed to afford iron(VI). Williams and Riley have already pointed out that iron(III) nitrate is the best source of ferric ions, probably because the nitrate ion is more stable toward oxidation by the ferrate ion than any of the other anions tried, which included chloride, sulfate, and phosphate ions.[34] Moreover, we have found that only analytical grade potassium hydroxide should be employed for preparing potassium ferrate. As large amounts of the base are needed, we have tried to use technical grade potassium hydroxide to reduce the cost of the process. However, these attempts led to a rapid decomposition of the ferrate ions and gave samples of very low purity. Reducing organic materials or metal traces that contaminate the low-purity hydroxide probably account for these results. Nickel(II) and cobalt(II) salts, for instance, are well-known catalysts for the decomposition of high-valent oxyanions. Ettel and Veprek-Siska have shown that the half-life of an alkaline ferrate solution is reduced by a factor of at least 40 when nickel(II) is added in micromolar concentration.[35,36]

The method that we have devised to purify our K_2FeO_4 samples is intermediate between those of Thompson *et al.*[32] and of Williams and Riley.[34] The crude ferrate is precipitated twice from chilled saturated aqueous potassium hydroxide solutions and rinsed successively with three organic solvents: (1) *n*-pentane to displace the residual water remaining on the filter, (2) methanol to dissolve the hydroxide, chloride, and nitrate impurities present, and (3) diethyl ether to accelerate the drying of the salt. The removal of excess water with an inert hydrocarbon is absolutely essential to the success of the purification. Failure to do it results in the rapid oxidation of methanol to formaldehyde and the associated reduction of ferrate to rust. We have replaced the carcinogenic benzene used in earlier procedures by volatile *n*-pentane, but cyclohexane, *n*-heptane, and toluene are equally suitable. Methanol was chosen rather than ethanol or 2-propanol, because it is a better solvent for potassium hydroxide and other mineral impurities.

Compared with the previous methods, our purification procedure is both faster and more efficient. It does not require multiple time-consuming suspending/filtering/washing cycles nor large volumes of organic solvents. Numerous samples were prepared in yields varying between 67 and 80% of the theoretical. Their purity, ascertained by the chromite titration method,[33] ranged between 97 and 99%.

Potassium Ferrate(VI) as an Oxidant

Potassium ferrate(VI) is a black-purple powder that remains stable in the air for long periods of time, provided that moisture is excluded. It is isomorphous with potassium sulfate, manganate, and chromate (K_2SO_4, K_2MnO_4, and K_2CrO_4). The ferrate dianion FeO_4^{2-} has a tetrahe-

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dral structure slightly distorted in the crystal state.[37] In aqueous solution, the ion remains monomeric, and its four oxygen atoms become equivalent and exchange slowly with the solvent.[38] In acidic or neutral solution, the ferrate ions are quickly reduced by water. Oxygen is evolved, and ferric complexes are formed, as summarized in eq 4. In basic solution, the rate of decomposition of ferrate is highly variable. pH and temperature are key factors, but light does not affect the stability of ferrate solutions.[39] In 1958, Wood observed that aqueous K_2FeO_4 was fairly stable around pH 10.[40] More recently, Lee and Gai have carried out precise kinetic measurements and found that, in dilute solution, the lowest rate of reduction of ferrate by water occurs between pH 9.4 and 9.7.[41] In strong alkali (3 M or above), ferrate solutions reach another region of stability, thus allowing the preparation and purification of potassium ferrate by the wet method.

$$4K_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 3O_2\uparrow + 8KOH \quad (4)$$

Potassium ferrate is insoluble in common organic solvents. It can be suspended in ether, chloroform, benzene, and other solvents without rapid decomposition. Alcohols may also be used, provided that they do not contain more than 20% water.[29] Above this limit, fast decomposition ensues, and aldehydes or ketones are formed. The reduction potentials for the Fe(VI)/Fe(III) couple have been estimated as 2.20 and 0.72 V versus NHE in acidic and basic solutions, respectively (eqs 5 and 6).[40] These values are significantly higher than those corresponding to the Mn(VII)/Mn(IV) [$E°(MnO_4^-/MnO_2)$ = 1.679 and 0.588 V at pH 1 and 14, respectively] or Cr(VI)/Cr(III) couples [$E°(Cr_2O_7^{2-}/Cr^{3+})$ = 1.33 V in acidic medium, $E°(CrO_4^{2-}/Cr(OH)_3)$ = −0.12 V in basic medium].[42] Thus, ferrates are expected to be more powerful oxidants than their manganese or chromium counterparts. Indeed, in 1897, Moeser observed that ammonia is oxidized by cold potassium ferrate solutions, whereas potassium permanganate solutions react only when hot.[29] Early investigators also noted that organic materials such as filter paper, ethanol, and wood were attacked by aqueous potassium ferrate.[29] During the 1960s, two contradictory reports about the possible use of potassium ferrate(VI) in organic synthesis were published,[43,44] but the first systematic study of the oxidation of organic compounds with K_2FeO_4 was carried out by Audette *et al.* in 1971. These authors reported the oxidation of alcohols and amines to the corresponding aldehydes or ketones using a solution of potassium ferrate in pure water or in water/dimethyl sulfoxide, -diglyme, or -dioxane mixtures.[45] They also gathered a few mechanistic indications,[46] later complemented by Schiopescu *et al.*[47] Tsuda and Nakajima oxidized a few allylic and benzylic alcohols in alkaline aqueous *tert*-butyl alcohol at room temperature,[48] whereas BeMiller *et al.* were able to selectively convert the primary hydroxymethyl groups of carbohydrates into aldehydes using K_2FeO_4 in aqueous sodium carbonate or phosphate solutions at 50 °C. In most cases, however, the main products after long reaction times were, perhaps, 3,6-hemiacetals or, more likely, dimers or higher polymers.[49] Closely related results were obtained by Williams and Riley when they heated potassium ferrate with polyols at 100 °C. An oxidation of the terminal hydroxyl groups initially occurred, but polymerization could not be avoided, and only complex tarry materials were isolated.[34] Besides alcohols and amines, only a few other functional groups were oxidized by potassium ferrate in aqueous media, among them sulfur derivatives[50] and hydrazines.[51]

$$FeO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O \quad (5)$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Fe(OH)_3(s) + 5OH^- \quad (6)$$

To further expand the scope of the oxidation to non-water-soluble substrates, Kim *et al.* used phase-transfer catalysis. They selectively oxidized allylic and benzylic alcohols to the corresponding carbonyl compounds using potassium ferrate at room temperature in benzene and aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride.[52] Another approach from the same group involved the recourse to a solid mixture of K_2FeO_4, basic alumina, and a hydrated inorganic salt such as $CuSO_4\cdot 5H_2O$ for oxidizing allylic and benzylic alcohols dissolved in benzene.[53] The roles of the solid support and of the metallic salt within this heterogeneous system were not investigated. The only indications available come from a related study of the oxidation of alcohols by a mixture of $KMnO_4$ and $CuSO_4\cdot 5H_2O$. It was assumed that the latter salt acted as a source of humidity.[54]

Results and Discussion

Oxidation of Benzyl Alcohol. To start our investigations on the oxidation of organic substrates with potassium ferrate in nonaqueous media, we have selected benzyl alcohol as a probe substrate (eq 7). This simple aromatic compound is particularly activated toward oxidation. The presence or not of benzoic acid along with benzaldehyde among the reaction products constitutes a simple selectivity test to assess the mildness of our oxidation procedure. Preliminary experiments had shown that hydrocarbons were promising solvents for the reaction. Thus, benzyl alcohol (2 mmol) and potassium

$$3PhCH_2OH + 2K_2FeO_4 \rightarrow 3PhCHO + Fe_2O_3 + 4KOH + H_2O \quad (7)$$

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Table 1. Comparison between Various Solid Catalysts for the Oxidation of Benzyl Alcohol with Potassium Ferrate in Cyclohexane

		benzaldehyde GC yield, %		
run	catalyst	2 h	8 h	24 h
1	none	1	14	44
2	acidic alumina	1	20	36
3	NaX zeolite	0	1	4
4	ZSM-5 zeolite	1	2	16
5	H-mordenite	7	42	49
6	ultrastable Y zeolite	56	67	90
7	ZF520 zeolite	64	95	98
8	K10 clay	57	94	99
9	silica gel	28	70	88
10	Japanese acidic clay	60	77	85
11	kaolin	7	24	50
12	$K10/H^+$ [a]	5	32	53
13	$K10/Cu^{2+}$ [a]	27	54	62
14	$FeCl_3/K10$[a]	7	33	62
15	$ZnCl_2/K10$[a]	3	19	62
16	$Al_2O_3 + CuSO_4{\cdot}5H_2O$[a]	1	7	87

[a] See text for details.

Table 2. Influence of the Catalyst Activation on the Oxidation of Benzyl Alcohol with Potassium Ferrate in Cyclohexane

		benzaldehyde GC yield, %		
run	catalyst[a]	2 h	8 h	24 h
1	none	1	14	44
2	dried K10[b]	1	2	9
3	crude K10	84	99	100
4	crushed K10[c]	94	92	100
5	K10, O_2[d]	83	99	100
6	H_2O	56	71	82

[a] All 1 g, except H_2O (0.13 g). [b] In a vacuum oven overnight at 40 °C under 1.5 mm Hg. [c] The reagent and the catalyst were crushed together in a mortar prior to the reaction. [d] Reaction under 1 atm of medical oxygen.

ferrate (5 mmol) were suspended in cyclohexane (30 mL), together with 1 g of a solid catalyst. The suspension was stirred 24 h at room temperature, and the supernatant solution was analyzed by GC at various stages. The results are gathered in Table 1. The solids tested can be classified in three groups according to the amounts of benzaldehyde produced. In the absence of any catalyst (run 1), or in the presence of acidic alumina, NaX, ZSM-5, or H-mordenite zeolites (runs 2−5), the yields are extremely low after 2 h and do not exceed 50% after 24 h. With the faujasite-type zeolites ultrastable Y (Si/Al > 100, run 6) and ZF520 (Si/Al = 20, run 7), or with the K10 montmorillonite clay, the Japanese acidic clay, and silica gel (runs 8−10), the oxidation proceeds much faster, and yields above 80% are reached after 8 or 24 h. Almost quantitative conversion of benzyl alcohol to benzaldehyde is achieved with the K10 clay and the ZF520 zeolite. The third group is intermediate between the two previous ones. Initial reaction rates are moderate, and final yields vary between 50 and 62%. This group includes the kaolin clay sample (run 11) and four modified clay catalysts: *viz.*, proton- or copper(II)-exchanged K10 clays (runs 12 and 13) and ferric chloride- or zinc chloride-impregnated K10 clays (runs 14 and 15). A control experiment using a solid mixture of basic alumina and copper(II) sulfate pentahydrate (0.5 g each), as recommended by Kim *et al.*,[53] was also carried out (run 16). Under our reaction conditions, however, this combination turned out to be a less efficient catalyst than various aluminosilicate solids or even silica gel.

No evidence of benzoic acid formation was found in any case, but small amounts of cyclohexanol and cyclohexanone resulting from the oxidation of the cyclohexane solvent were detected by GC after 24 h of reaction in the presence of K10 montmorillonite clay, Japanese acidic clay, and copper(II)-exchanged K10 clay. We shall discuss later the significance of these observations.

As the K10 clay seemed to be the best catalyst among the solids tested, we have launched a systematic study of the oxidation of benzyl alcohol in the presence of this inexpensive industrial acidic clay. First, we have examined the solid reagent itself in order to determine the best way to prepare it and to activate it. Instead of mixing the clay and the inorganic salt immediately prior to the oxidation, we have tried to prepare clay-impregnated potassium ferrate either by oxidizing clay-supported ferric nitrate (“clayfen”) with an alkaline hypochlorite solution or by precipitating potassium ferrate in a suspension of the clay. The first approach failed to afford any iron(VI)-containing reagent. Suspending clayfen in a concentrated aqueous solution of KOH and KOCl indeed led to the formation of ferrate ions, as evidenced by the appearance of a black-purple color, but the resulting mud could not be filtered off and dried without complete reduction of the iron(VI) into ferric oxide. The water that remains adsorbed on the clay even after careful filtration probably accounts for this decomposition. The second approach involved slow addition of a solution of potassium ferrate in 3 M aqueous KOH to a vigorously stirred suspension of K10 clay in a large volume of ethanol. An intimate mixture of the two solid components resulted, which could be filtered off and dried without apparent decomposition. Although the iron(VI) content of such a material was not determined, it must, nevertheless, be low, and only disappointing yields of benzaldehyde were obtained in the test reaction with benzyl alcohol. Thus, the recourse to clay-supported potassium ferrate did not bring any significant improvement to the process, and we decided to use only simple mixtures of the two solid partners for all subsequent experiments.

Yet, the influence of grinding them together in a mortar prior to the reaction was investigated, as can be seen from the data in Table 2. The powder obtained by crushing K_2FeO_4 and K10 clay reacted slightly faster with benzyl alcohol than the two ingredients added separately, but almost quantitative yields of benzaldehyde were obtained within 8 h in both cases (compare entries 3 and 4). After 24 h, the reaction was complete, and the oxidation of cyclohexane had begun. Because ground potassium ferrate is more prone to decomposition by air moisture and sticks to the mortar and pestle, we were concerned that grinding the solid mixture would randomly reduce the amount of oxidant introduced in a reaction while only slightly increasing the oxidation rate. Thus, we have abandoned this procedure.

In another attempt to further activate the solid reagent, we have thoroughly dried the crude K10 clay in a vacuum oven before using it to catalyze the oxidation of benzyl alcohol in cyclohexane at room temperature. Dehydration led to an 11% mass loss and had a tremendous influence on the outcome of the oxidation: only 9% of benzaldehyde was obtained after 24 h (entry 2), less than in the absence of any catalyst (entry 1). This seemingly surprising result is consistent with earlier observations from Menger and Lee. In an attempt to duplicate previous experiments on the oxidation of cyclododecanol with $KMnO_4$-coated molecular sieves in benzene,[55] they initially obtained erratic results, which were eventually associated with the humidity content of the solid oxidizer.[54] They found that drying the reagent over phosphorus pentoxide completely inhibited the formation of cyclododecanone but that the water levels required for an optimum reaction were small, in the range of a few microliters per milliliter of benzene. The presence of a small amount of water also increased the rate of heterogeneous Wittig and Wittig−Horner reactions in the presence of alumina or alumina-supported potassium fluoride, as evidenced by Foucaud *et al.*,[56] and very recently, Posner *et al.* stressed the crucial importance of humidity in the preparation of chiral binaphthol−titanium complexes. The moisture content of their molecular sieve promoter had to fall within a very narrow specific range (15−17%) in order to achieve high, reproducible enantioselectivities.[57]

To give further insight into the role of moisture on our system, a control experiment was performed with a mixture of potassium ferrate (1 g) and the amount of water corresponding approximately to that in 1 g of crude K10 clay (0.13 g). It gave results intermediate between those obtained in the presence of dry and crude clays (Table 2, entries 2, 3, 6). Thus, the aluminosilicate solid not only acts as a source of humidity but also displays an intrinsic catalytic activity. The intervention of the strong Brønsted or Lewis acidic centers present within the aluminosilicate structure first comes to mind when trying to account for this catalytic activity. However, the good results obtained with silica gel, which lacks any specific acidity, or the similar behavior of the modified clay catalysts goes against this hypothesis (*cf.* Table 1). It is particularly striking to note that the catalysts prepared by impregnating the K10 clay with zinc or ferric chloride, or by exchanging its cations with protons or copper(II) ions, lead to similar yields of benzaldehyde, though their acidic sites must differ in nature and strength. The thermal treatment involved in the preparation of these materials, which in turn controls their dehydration, is more likely to be responsible for the yield discrepancies between the crude K10 clay and its modified derivatives. However, we did not further investigate the correlation between the hydration level and the activity of our catalysts.

With acidity ruled out, the most plausible function of the K10 clay is to provide a polar microenvironment which would both enhance the reactivity of the adsorbed species and increase their encounter rate. The polar nature of the oxidation of benzyl alcohol with potassium ferrate in the presence of microporous adsorbents has been evidenced by various experiments. A radical mechanism involving the transfer of a hydrogen atom ($H^{\bullet}$) from a substrate to a metal active site has recently been proposed by Gardner and Mayer for the oxidation of toluene with permanganate in the neat hydrocarbon. The intermediacy of benzylic radicals was postulated, based on kinetics data and the fact that MnO_4^- reacts about 5 times faster when the toluene solution is saturated with oxygen.[58] Radical intermediates have also been proposed in the oxidation of alcohols with ferrate ions in alkaline aqueous solutions.[41,46] Although clays are known to initiate redox reactions by oxidizing organic molecules to radicals and radical cations,[59] such a pathway is very unlikely to occur in our system. In the presence of the K10 clay, identical results were obtained whether the oxidation of benzyl alcohol with K_2FeO_4 was carried out under a normal atmosphere or under oxygen (Table 2, entries 3 and 5). In another already-mentioned experiment (Table 1, run 3), the catalytic activity of the NaX faujasite was investigated. Such a zeolite has previously been used successfully in our laboratory to catalyze heterogeneous radical aromatic chlorinations by sulfuryl chloride.[60] It fails, however, to afford any significant amount of oxidation products when used in conjunction with potassium ferrate, even under high-temperature and intense visible light conditions. Hence, we assume that a polar reaction mechanism takes place on the K10 clay surface. The charged layered structure of the aluminosilicate solid provides, indeed, a suitable, highly polar environment to adsorb benzyl alcohol from the bulk of the hydrophobic cyclohexane solvent and to favor its encounter with ferrate ions generated in the hydrated interlamellar spaces.[61]

Table 3. Influence of the Relative Amounts of Potassium Ferrate and of the K10 Clay on the Oxidation of Benzyl Alcohol in Cyclohexane

amount of K_2FeO_4, g	amount of K10 clay, g	benzaldehyde GC yield, % 2 h	4 h	8 h	24 h
1	0.1	10	13	23	43
1	0.5	50	59	65	81
1	1	84		99	100
1	2	100	100	100	100
0.5	1	81	93	97	99

To continue our systematic study of the oxidation of benzyl alcohol and to further appraise the influence of the K10 clay on the outcome of the reaction, we have modified the relative ratios of reagents and catalyst (Table 3). While maintaining a 2.5 molar excess of potassium ferrate (1 g, 5 mmol) to benzyl alcohol (2 mmol), the amount of K10 montmorillonite was varied between 0.1 and 2 g. The results are clear-cut: within the range under scrutiny, the rate of benzaldehyde formation steadily increases with the quantity of clay used (Figure 1). Adding only a trifling amount of catalyst is obviously not appropriate in this case, and 1:1 or 2:1 K10 clay:K_2FeO_4 weight ratios are required in order to achieve a quantitative conversion of benzyl alcohol within a few hours. On the other hand, we were able to reduce the quantity of the ferrate salt employed from 1 to 0.5 g (2.5 mmol) without any significant consequence. This corresponds to a 1.25 molar ratio between potassium ferrate and benzyl alcohol and to a stoichiometric ratio of *ca.* 2 according to eq 7. This result is very gratifying, knowing that 10-fold or even larger excesses of high-valent metal salts are commonly involved in standard oxidation procedures.[2] It should also be pointed out that the overoxidation of benzaldehyde to benzoic acid was never an issue in these experiments. Once the conversion of benzyl alcohol is complete, varying the amounts of catalyst and oxidant affects only the time after which cyclohexanol and cyclohexanone start to appear.

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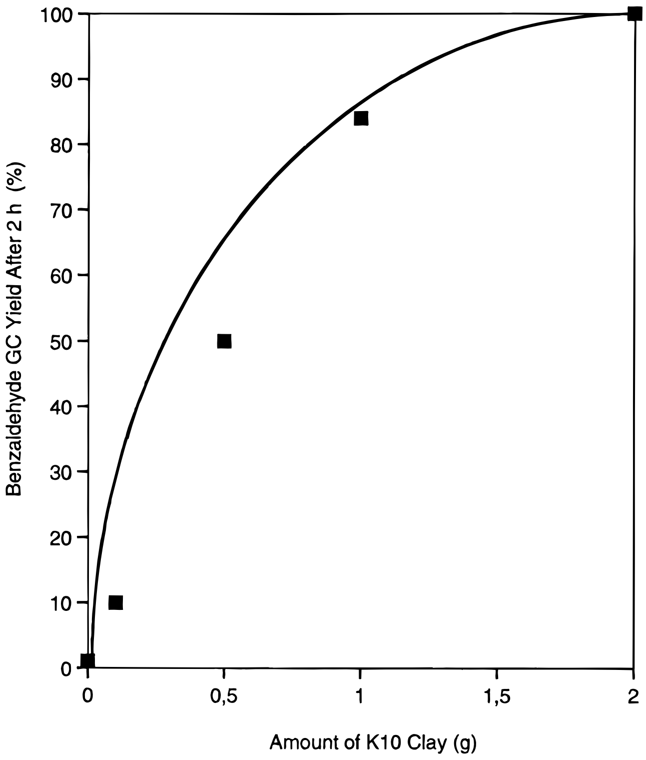

Figure 1. Influence of the amount of K10 clay on the oxidation of benzyl alcohol with potassium ferrate.

Table 4. Oxidation of Benzyl Alcohol by Potassium Ferrate in Various Solvents Using the K10 Clay as a Catalyst

		benzaldehyde GC yield, %			
run	solvent	2 h	4 h	8 h	24 h
1	dichloromethane	29	49	61	72
2	chloroform	22	30	38	40
3	diethyl ether	2	6	27	42
4	*tert*-butyl methyl ether	9	23	33	64
5	acetonitrile	16	19	34	45
6	carbon disulfide	63	67	73	78
7	benzene	59	73	82	99
8	toluene	54	75	90	99
9	*n*-pentane	82	92	99	100
10	*n*-hexane	80	87	100	100
11	cyclohexane	81	89	99	100

To avoid these side reactions, we have replaced cyclohexane with a number of other common organic solvents (Table 4). Alcohols such as methanol and ethanol were excluded from our tests, because of their high susceptibility toward oxidants, but other functional group-containing molecules were investigated. They include two chlorinated derivatives (dichloromethane and chloroform) and two ethers (diethyl ether and *tert*-butyl methyl ether), as well as acetonitrile and carbon disulfide (entries 1−6). None of these polar solvents afforded quantitative yields of benzaldehyde, even after 24 h of reaction. Benzene, which was the nonaqueous solvent of choice in earlier oxidation procedures with K_2FeO_4 or $BaFeO_4 \cdot H_2O$,[16,53] and toluene have similar influences on the outcome of the reaction and lead to an almost complete conversion of benzyl alcohol in benzaldehyde within 24 h (entries 7 and 8). However, the best results are obtained when working with saturated aliphatic hydrocarbons. Taking into account the experimental errors, identical yields are obtained whether *n*-pentane, *n*-hexane, or cyclohexane is used. In these liquids, the yield of benzaldehyde reaches 80% after 2 h, 90% after 4 h, and 100% after 8 h (entries 9−11). Indisputably, alkanes are excellent solvents for the oxidation of benzyl alcohol with potassium ferrate and K10 clay in nonaqueous media. Their hydrophobic nature might be responsible for this situation. In a heterogeneous biphasic mixture of clay and a liquid alkane, benzyl alcohol and water molecules are more likely adsorbed on the highly polar clay surface and do not migrate in the bulk of the solution. Thus, the solid support can fully play its role of reduced dimensionality reaction space. In more polar solvents, the reaction partners are distributed between the solid and the liquid phases, thus decreasing the probability of successful collisions.

Table 5. Influence of Temperature on the Oxidation of Benzyl Alcohol with Potassium Ferrate Using the K10 Clay as a Catalyst in *n*-Heptane

	benzaldehyde GC yield, %			
temperature	1 h	2 h	4 h	8 h
0 °C	32	48	65	73
rt (± 22 °C)	64	73	81	90
50 °C	78	89	94	98

Except for carbon disulfide, which became yellowish after 3 days in contact with the solid mixture, no other solvent showed visible signs of degradation in the presence of K10 clay and potassium ferrate, even when left for a few days at room temperature. Special attention was paid to the GC analyses of the reaction mixtures based on *n*-pentane and *n*-hexane. In both cases, small peaks whose retention times fall in the same range as those for the isomers of C_5 or C_6 alkanols and alkanones were detected. Although these byproducts have not been formally characterized, it should be stressed that their detection was made possible only because of the high sensitivity of the capillary GC technique adopted. Yet, they are present in minute amounts. To give an idea, the uncorrected areas of these peaks represent less than 0.4% of the benzaldehyde peak. Thus, *n*-pentane and *n*-hexane are essentially inert under our reaction conditions. Cyclohexane, on the contrary, is attacked to a much larger extend by the solid oxidant. As has already been mentioned repeatedly, significant amounts of cyclohexanol and cyclohexanone are formed when the parent hydrocarbon serves as the solvent. The integration of the chromatograms obtained under these conditions indicates that the peaks corresponding to the oxidation of the solvent represent up to 15% of the benzaldehyde peak area if the reaction time is prolonged long enough. Again, this raw, uncorrected percentage is given only as an indication. More precise figures will be discussed later in the text, when we set about the oxidation of hydrocarbons.

First, we have examined the influence of the temperature on the oxidation of benzyl alcohol (2 mmol) with potassium ferrate (1 g) in the presence of the K10 clay (1 g). Results from the previous set of experiments have shown that *n*-pentane and *n*-hexane were excellent solvents for performing the oxidation of the model alcohol at room temperature. We preferred, however, to use *n*-heptane, because of its higher boiling point. Four reactions were carried out at 0 °C, at ambient temperature (~22 °C), at 50 °C, and under reflux conditions (~98 °C). Between 0 and 50 °C, the rate of oxidation increases regularly with the temperature as expected (Table 5). Besides benzaldehyde, a number of other byproducts are also detected by GC. Their retention times suggest that they result from the oxidation of the solvent, and their intensities remain smaller than 1% of the benzaldehyde signal. The experiment conducted under reflux leads to

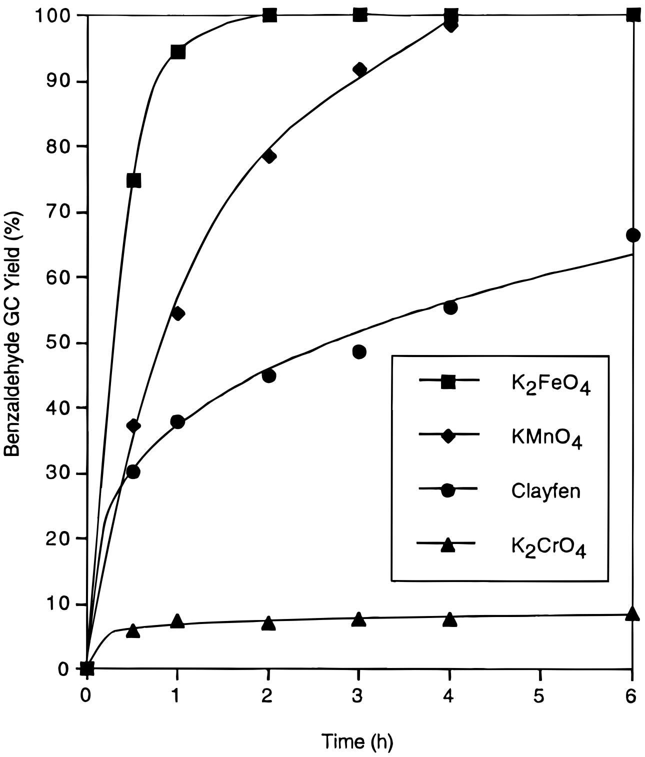

Figure 2. Time evolution of the oxidation of benzyl alcohol by various solid oxidizers in cyclohexane using K10 clay as a catalyst.

a totally different result. Benzyl alcohol is fully consumed within 1 h but affords only a minor proportion of benzaldehyde. The major products have higher molecular weights and form a complex mixture, out of which only dibenzyl ether was identified with certainty. It has been confirmed by GC and IR analyses that benzoic acid was not formed. Therefore, the change of reaction pathway does not correspond to an overoxidation of the substrate, but most probably to dehydration and condensation reactions catalyzed by the acidic clay at elevated temperatures. Our concern was to avoid oligomer or polymer formation. We have not further investigated this topic which had been studied at length by the group in Swansea in the 1980s, using clays to generate ethers from alcohols.[62]

To conclude our study of the oxidation of benzyl alcohol under heterogeneous conditions, we have compared the power of potassium ferrate(VI) with those of its chromium(VI) and manganese(VII) congeners, potassium chromate and permanganate. To allow a direct comparison of the results, all the reactions were run in cyclohexane (30 mL) at room temperature using 2 mmol of benzyl alcohol (0.216 g), 5 mmol of oxidant (K_2FeO_4, 0.990 g; K_2CrO_4, 0.971 g; $KMnO_4$, 0.790 g), and 2 g of K10 clay. In each case, the solid mixture was crushed in a mortar immediately prior to the reaction in order to level the different granularities of the inorganic salts. An additional experiment was performed in the presence of the clay-supported iron(III) reagent clayfen. Due to the mode of preparation of this reagent,[11] the weight and molar ratios of the reagents and catalyst had to be modified. Thus, 2 g of the clay-supported ferric nitrate was reacted, and the actual batch content for iron(III) was 2.3 mmol. Figure 2 depicts the time evolution of the benzaldehyde yields using the four solid oxidants. The superiority of potassium ferrate is blatant. With the 2:1 clay-to-ferrate ratio adopted, the reaction is quantitative within 2 h, and cyclohexane oxidation begins after this period. Potassium permanganate is the second best choice. The 6 h imparted to the reaction is needed to achieve a total conversion of benzyl alcohol, but traces of cyclohexanol and cyclohexanone are detected in the last sample withdrawn and analyzed. The reaction with potassium chromate, on the other hand, is sluggish and does not afford any satisfactory yield after 6 h. Clayfen rapidly converts benzyl alcohol to a nitrous ester,[63] as evidenced by GC analysis, but subsequent transformation of this intermediate to benzaldehyde occurs slowly at room temperature.

Oxidation of Alcohols. We have tested on substrates other than benzyl alcohol the generality of our oxidation procedure. In view of the results gathered in Table 3 and Figure 1, a 2:1 or 2.5:1 weight ratio of K10 clay relative to K_2FeO_4 was chosen, with a 2-fold molar excess of the oxidizer over the organic substrate (10 and 5 mmol, respectively). *n*-Pentane (50 mL) was chosen as the solvent, and the reactions were carried out at room temperature. The recourse to heterogeneous conditions and the choice of a low-boiling point hydrocarbon as the reaction medium, together with that of the more polar diethyl ether as the workup solvent, greatly simplified and sped-up the isolation procedure. Indeed, it was only necessary to filter off the spent solid at the end of the reaction, wash it with a few portions of ether, and evaporate the resulting filtrate to obtain rather pure final product.

Various alcohols were oxidized under these conditions (Table 6). A single product was obtained in all cases, except with benzoin, which underwent an oxidative cleavage into benzaldehyde, besides its oxidation to benzil (entry 1). Other aromatic alcohols bearing an hydroxyl group α to the ring, as well as the related cinnamyl alcohol, reacted quantitatively within a few hours at room temperature (entries 2−7). The corresponding aldehydes or ketones were usually isolated in high yields. However, full recovery of benzaldehyde and of furfuraldehyde was not achieved. Washing the spent solid reagent with polar solvents such as acetone or methanol did not improve the weight balance. Degradation or polymerization of these sensitive compounds on the surface of the acidic clay probably accounts for loss of organic materials. Among the aliphatic alcohols tested, only 3-methyl-2-cyclohexen-1-ol reacted almost completely within 4 h (entry 8). Two other allylic alcohols, *viz.*, 2-cyclohexen-1-ol and 2-methyl-1-penten-3-ol, gave more disappointing yields, although the reaction time was extended to 24 h (entries 9 and 10). The reaction of unactivated secondary alcohols like cyclohexanol, 4-*tert*-butylcyclohexanol, and fenchyl alcohol was very sluggish (entries 11−13), but borneol was converted to camphor in 82% isolated yield after 24 h (entry 14).

It is noteworthy that some of the alcohols tested were not fully soluble in *n*-pentane and led to heterogeneous liquid−liquid (entries 5 and 10) or liquid−solid (entries 1, 6, and 7) biphasic mixtures. However, despite their limited solubilities, most of these substrates were fully consumed within a few hours.

Oxidative Coupling of Thiols. The performance as an oxidant of potassium ferrate toward thiols was studied

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Table 6. Oxidation of Alcohols with Potassium Ferrate in *n*-Pentane Using the K10 Clay as a Catalyst

run	substrate	product	reaction time, h	conversion,[a] %	isolated yield, %
1	benzoin	benzil[b]	2	100	36
2	benzyl alcohol[c]	benzaldehyde	3	100	63
3	1-phenylethanol	acetophenone	2.5	100	98
4	benzhydrol[d]	benzophenone	2	100	100
5	furfuryl alcohol	furfuraldehyde	4	94	51
6	1-indanol	1-indanone	3	99	76
7	cinnamyl alcohol	cinnamaldehyde	2	100	88
8	3-methyl-2-cyclohexen-1-ol	3-methyl-2-cyclohexen-1-one	4	96	70
9	2-cyclohexen-1-ol	2-cyclohexen-1-one	24	88	50
10	2-methyl-1-penten-3-ol	2-methyl-1-penten-3-one	24	67	11
11	cyclohexanol	cyclohexanone	24	51	26
12	4-*tert*-butylcyclohexanol	4-*tert*-butylcyclohexanone	96	64	19
13	fenchyl alcohol[c]	fenchone	24	29	25
14	borneol[c]	camphor	24	93	82

[a] Monitored by GC or by TLC. [b] Benzaldehyde is also formed. [c] 5 g of K10 clay used. [d] Solvent was benzene.

Table 7. Coupling of Thiols into Disulfides with Potassium Ferrate in *n*-Pentane Using the K10 Clay as a Catalyst

substrate	product	reaction time, h	conversion,[a] %	isolated yield, %
2-propanethiol	diisopropyl disulfide	1	100	75
1-butanethiol	di-*n*-butyl disulfide	0.5	100	92
2-methyl-2-propanethiol	di-*tert*-butyl disulfide	2	99	70
cyclohexanethiol	dicyclohexyl disulfide	1.5	100	97
thiophenol	diphenyl disulfide	0.25	100	85
benzyl mercaptan	dibenzyl disulfide	0.5	100	93
2,4,5-trichlorothiophenol[b]	bis(2,4,5-trichlorophenyl) disulfide	0.5	100	88

[a] Monitored by GC. [b] Workup solvent was $CHCl_3$.

Table 8. Oxidation of Nitrogen-Containing Organic Substrates with Potassium Ferrate in *n*-Pentane Using the K10 Clay as a Catalyst

substrate	product	reaction time, h	isolated yield, %
aniline[a]	azobenzene	8	63
benzylamine	benzaldehyde	3	85
cyclohexanone oxime	cyclohexanone	2	73
acetophenone oxime	acetophenone	3	82
benzophenone oxime	benzophenone	3	70
acetophenone tosylhydrazone	acetophenone	2	64
acetophenone phenylhydrazone	acetophenone	8	57
acetophenone (2,4-dinitrophenyl)hydrazone	acetophenone	24	10

[a] Freshly distilled prior to use.

in the presence of the K10 clay. These experiments were carried out by reacting 5 mmol of a thiol dissolved in *n*-pentane (or suspended in the case of 2,4,5-trichlorothiophenol) with 10 mmol of K_2FeO_4 and 4 g of K10 clay at room temperature. A rapid reaction ensued, which led to the corresponding symmetrical disulfides resulting from oxidative coupling with good to excellent yields (Table 7). The case of thiophenol is of particular interest, because its coupling into diphenyl disulfide is a convenient reactivity test for supported oxidizing reagents.[11] Under our conditions, the coupling product was isolated in 85% yield after 15 min of reaction. Although more than satisfactory, this result is inferior to that from use of clayfen under similar conditions, as the clay-supported iron(III) reagent afforded a 97% yield of diphenyl disulfide within 10 min.[64] With deactivated substrates, however, recourse to the iron(VI) oxidizer sharply improved the outcome of the reaction. Thus, for instance, *tert*-butyl mercaptan failed to react with clayfen even under reflux, and isopropyl mercaptan led only to a 39% isolated yield of the corresponding disulfide.[64] Here, with the K_2FeO_4/K10 solid mixture, isolated yields climbed to 70 and 75% respectively after 2 and 1 h of reaction. Comparison of the reaction times needed to reach completion in the cases of these two thiols and of the linear *n*-butyl mercaptan shows that the ease of coupling decreases in the order primary > secondary > tertiary for aliphatic thiols, in accordance with previous reports.[65]

Oxidation of Nitrogen Derivatives. To further enlarge the scope of the potassium ferrate/K10 clay solid reagent, we have examined oxidation of various nitrogen-containing derivatives using different experimental procedures (Table 8). Aniline and benzylamine were oxidized with the conditions setup for alcohols and thiols. With aniline, a coupling occurred, and diazobenzene was the sole isolated product. Several washings with diethyl ether were necessary in order to desorb the dye from the solid support, leading to a decent 63% yield after 8 h. With benzyl amine, benzaldehyde was the sole product formed at ambient temperature, in 85% yield. The reaction was complete within 3 h, the same period necessary for the parallel oxidation of benzyl alcohol. In another experiment under reflux conditions, the aldehyde reacted immediately with the remaining substrate, so the corresponding Schiff base, *N*-benzylbenzaldimine, was the main product isolated.

Three oximes were also subjected to oxidation by the K_2FeO_4/K10 mixture in *n*-pentane. Regeneration of the parent ketone (*viz.*, cyclohexanone, acetophenone, or benzophenone) took place within 2−3 h. Yields were consistently high, but the crude aromatic ketones had to be purified by column chromatography to attain a satisfactory level of purity.

Hydrazones are another important class of nitrogen-containing derivatives, and their cleavage into aldehydes or ketones has been performed with a variety of oxidizing agents.[66] The quantitative yield of acetophenone obtained while oxidizing 1-phenylethanol (*cf*. Table 6) and the good result obtained in the deprotection of acetophenone oxime encouraged us to elect this molecule as a

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Table 9. Oxidation of Hydrocarbons with Potassium Ferrate at 75 °C Using the K10 Clay as a Catalyst

		GC yield,[a] %, and (product distribution)		
substrate	products	24 h	48 h	72 h
adamantane[b]	1-adamantanol, 2-adamantanol + 2-adamantanone[c]	11 (70:30)	22 (83:17)	38 (91: 9)
cyclohexane	cyclohexanol, cyclohexanone	9 (58:42)		14 (51:49)
cycloheptane	cycloheptanol, cycloheptanone	34 (39:61)	35 (40:60)	35 (40:60)
cyclooctane	cyclooctanol, cyclooctanone	25 (28:72)	29 (30:70)	30 (32:68)
toluene	benzyl alcohol, benzaldehyde	11 (17:83)	13 (23:77)	14 (24:76)

[a] Based on ferrate ions. [b] 80 mmol in 50 mL of CCl_4. [c] 1-Chloroadamantane was also formed in significant but undetermined yields.

suitable carbonyl compound to regenerate from its hydrazones. Thus, we prepared three of the most common acetophenone hydrazone derivatives, *viz*., the tosylhydrazone, the phenylhydrazone, and the (2,4-dinitrophenyl)hydrazone. Next, we submitted these compounds (2.5 mmol) to oxidation by a 2-fold excess of potassium ferrate (1 g, 5 mmol) in the presence of K10 clay (2 g). *n*-Pentane served as the solvent for these reactions, although it did not dissolve the highly polar substrates. Common empirical knowledge in the area of solid-supported reagents, together with evidence gathered during the course of this work, indicates that solubility of the organic *products* rather than that of the *substrates* determines the success of an heterogeneous reaction. Nevertheless, the hydrazones appeared to be much more refractory to deprotection than the corresponding oxime. The cleavage of the tosylhydrazone and of the phenylhydrazone afforded acetophenone in moderate isolated yields after 2 and 8 h respectively, while the more stable (2,4-dinitrophenyl)-hydrazone remained largely unaffected under our reaction conditions, even after 24 h.

Oxidation of Hydrocarbons. The selective oxidation of hydrocarbons is of prime importance from both academic and industrial points of view.[67] The reagents or catalysts in these processes are often transition metal species.[68] It has been known for over a century that chromyl compounds[69] (*e.g.*, CrO_2Cl_2, $CrO_2(NO_3)_2$, and $CrO_2(OCOCF_3)_2$), permanganate,[70] and iron–oxo complexes (for instance, in cytochrome P-450 enzymes[71]) oxidize alkanes and arylalkanes. To the best of our knowledge, however, the use of potassium ferrate to oxidize C–H bonds has not been reported yet.

While oxidizing benzyl alcohol in cyclohexane solutions, we first became aware of the potential of K_2FeO_4 as a suitable reagent to functionalize hydrocarbons. A quantitative study of the oxidation of various cycloalkanes and of toluene has been undertaken. In these experiments, the substrates served as their own solvents (50 mL). Potassium ferrate (2 g, 10 mmol) and K10 clay (4 g) were added, together with a small amount of an appropriate linear alkane (0.3 g) serving as a GC internal standard. This was possible because *n*-alkanes are less prone to oxidation than their cyclic counterparts (*cf.* discussion of Table 4) and remain inert when the latter are introduced in huge excess. The suspensions were stirred at 75 °C for 3 days in well-stoppered flasks and analyzed at regular intervals. The results are gathered in Table 9. Cyclohexane, cycloheptane, and cyclooctane afforded the corresponding alcohols and ketones. Toluene was oxidized in benzyl alcohol and benzaldehyde, but no benzoic acid was detected. Although extended reaction times were needed and the yields remained below 50%, these results are deemed more than satisfactory, keeping in mind the low reactivity of the C–H bond. The most gratifying results were obtained with cycloheptane: the yield of oxidation products, based on ferrate ions, reached 35%, and the reaction was complete in less than 2 days. Except in the case of cyclohexane, which led to the reverse evolution, the alcohol/ketone ratio slightly increased with the reaction time. We are presently determining if the alcohol is the primary oxidation product and gives slowly the ketone due to further oxidizing under the reaction conditions.

We have also investigated the reaction of adamantane with potassium ferrate in the presence of the K10 clay. Because of the solid nature of this hydrocarbon, a suitable solvent had to be used. Other liquid alkanes were rejected because of their possible reaction when introduced as the main constituent of the reaction mixture. Perfluorohexane[72] was envisaged as an alternative, but no reaction occurred between adamantane (50 mmol) and potassium ferrate (10 mmol) suspended in this medium (50 mL) and heated to 50 °C in the presence of K10 clay (4 g). Under similar conditions, recourse to benzene as the solvent afforded only a 4% yield of oxygenated derivatives of adamantane after 3 days at 75 °C. A third trial in tetrachloromethane was more successful. Decent yields of oxidation products were obtained within 3 days at 75 °C (see Table 9). Adamantane was attacked mainly on its tertiary carbons, leading to the formation of 1-adamantanol, but smaller amounts of 2-adamantanol and 2-adamantanone resulting from the substitution of a methylene group were also obtained. These two products could not be fully separated by gas chromatography, but the ketone was present in a much higher proportion than the alcohol. 1-Chloroadamantane was also formed in significant amount, but the yield was not determined. A more detailed study of the oxidation of hydrocarbons with potassium ferrate has been launched and will be reported in a future publication.

Experimental Section

General Information. All the organic substrates and solvents were commercial products of the highest purity available, used without any further purification. Potassium ferrate was prepared as described below from analytical grade KOH (Baker Analyzed Reagent) and $Fe(NO_3)_3{\cdot}9H_2O$ (Acros), potassium chromate and permanganate were analytical grade reagents purchased from UCB, and clayfen was prepared according to the published procedure.[11] The following solids were used as catalysts: acidic aluminum oxide type 504C

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[67] (a) *Selective Hydrocarbon Activation, Principles and Progress*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990. (b) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989. (c) Hucknall, D. J. *Selective Oxidation of Hydrocarbons*; Academic Press: New York, 1974.

[68] (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, 1984. (b) *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. I., de Jonge, C. R. H. I., Eds.; Plenum: New York, 1986.

[69] (a) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7139–7156; (b) **1994**, *116*, 1855–1868 and references cited therein.

[70] Fatiadi, A. J. *Synthesis* **1987**, 85–127.

[71] *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1985.

[72] Tetradecafluorohexane, marketed as Perfluoro-compound FC-72 or Fluorinert Liquid FC-72 (Acros).

(Fluka), activated basic aluminum oxide (Aldrich), silica gel 70−230 mesh, 60 Å for column chromatography (Acros), XF-32 Airfloat kaolin (Freeport), Japanese acidic clay (Wako Pure Chemical Industries), and K10 montmorillonite clay (Süd-Chemie[73]). Ion-exchanged[74] and $FeCl_3$[75] - or $ZnCl_2$[76] -impregnated clays were prepared according to literature procedures. Zeolite powder NaX (13X) was purchased from Aldrich, zeolite ZF520 was a gift from Zeocat (Montoir de Bretagne), and other zeolites were gift samples from the Catholic University of Leuven, Belgium.

Analyses of products were performed on a Varian Star 3400CX/4400 chromatographic system equipped with a flame ionization detector and a capillary column (30 m length, 0.32 mm i.d., stationary phase DB5, 0.25 μm film thickness). Product identifications were performed by comparing retention times and IR spectra with those of authentic commercial samples.

Preparation of Potassium Ferrate. A solution of KOH (120 g) in 200 mL of water was chilled, and 60 g of chlorine (generated from 53.4 g of $KMnO_4$ and 330 mL of concentrated HCl[77]) was slowly bubbled over a 1.5 h period at 0 °C. Next, 180 g of KOH was added, and the resulting suspension was cooled to 0 °C. The precipitated KCl was removed by filtration through fritted glass. To the alkaline hypochlorite filtrate, vigorously stirred in an ice bath, was added 75 g of $Fe(NO_3)_3\cdot 9H_2O$ portion-wise in 1 h. Stirring was continued for an additional hour at 0 °C before 120 g of KOH was added in small portions. The resulting dark purple slurry was cooled to 0 °C and filtered through a coarse-porosity fritted glass with suction. The filtrate was discarded, and the precipitate was leached with six successive 50 mL portions of cold 1 M aqueous KOH. The leachings were quickly drawn each time through the filter into a filtering flask containing 600 mL of a chilled saturated KOH solution. The content of the flask was stirred for 20 min at 0 °C and filtered through a medium-porosity fritted glass with suction. Four 50 mL portions of *n*-pentane were flushed through the filter to force any residual water out of the fritted glass. (**Caution**: this step is crucial, as aqueous ferrate reacts readily with alcohols, so K_2FeO_4 is destroyed if it is not thoroughly dried before washing with methanol.) The crude ferrate was then quickly washed four times with 50 mL of methanol and twice with 50 mL of diethyl ether. It was dried under vacuum.

The sample was further purified by dissolving in 60 mL of cold 3 M aqueous KOH and quickly pouring into 250 mL of a chilled saturated KOH solution. The resulting suspension was stirred for 20 min at 0 °C. It was filtered through a medium-porosity fritted glass with suction, and the solid was rinsed four times with 30 mL of *n*-pentane (see above caution), four times with 30 mL of methanol, and twice with 30 mL of diethyl ether. It was then dried under vacuum. The product was a stable, homogeneous black powder, which could be stored for extended periods of time in a desiccator over P_2O_5 without noticeable decomposition.

Numerous samples were prepared by this method. The purity of K_2FeO_4, as analyzed by the chromite method,[33] was always higher than 97%. Typical yields ranged between 70 and 80% of the theoretical.

Oxidation of Benzyl Alcohol (Test Reaction): Typical Procedure. Unless otherwise stated in Tables 1−5, 1 g of K_2FeO_4 (5 mmol) and 1 g of a solid catalyst were added to 0.216 g of benzyl alcohol (2 mmol) in 30 mL of cyclohexane. The suspension was stirred for 24 h at room temperature, and the supernatant solution was analyzed by GC at regular intervals, assuming that benzyl alcohol and benzaldehyde had similar flame ionization detection coefficients.

Oxidation of Alcohols: General Procedure. Unless otherwise stated in Table 6, 2 g of K_2FeO_4 (10 mmol) and 4 g of K10 clay were added to 5 mmol of an alcohol in 50 mL of *n*-pentane. The suspension was stirred at room temperature, and the reaction was monitored by GC or by TLC. When no more evolution occurred, the solid reagent was filtered off with suction and washed with 3 × 20 mL of diethyl ether. The filtrates were combined and evaporated under reduced pressure to afford the products.

Coupling of Thiols: General Procedure. To 5 mmol of a thiol in 50 mL of *n*-pentane were added 2 g of K_2FeO_4 (10 mmol) and 4 g of K10 clay. The suspension was stirred at room temperature until completion of the reaction, as monitored by GC (see Table 7 for reaction times). The solid reagent was then filtered off with suction and washed with 3 × 20 mL of diethyl ether. The filtrates were combined and evaporated under reduced pressure to afford the products.

Oxidation of Amines and Oximes: General Procedure. To 5 mmol of an amine or an oxime prepared according to the standard method[78] in 50 mL of *n*-pentane were added 2 g of K_2FeO_4 and 4 g of K10 clay. The suspension was stirred at room temperature until completion of the reaction (see Table 8 for reaction times). The solid reagent was then filtered off with suction and washed with 3 × 20 mL of diethyl ether. The filtrates were combined and evaporated under reduced pressure to afford the products. In the case of acetophenone and benzophenone oximes, further purification by column chromatography on silica gel using benzene as eluent was necessary to obtain the pure ketones.

Cleavage of Acetophenone Hydrazones: General Procedure. To 2.5 mmol of an acetophenone hydrazone derivative prepared according to the standard procedure[78] suspended in 50 mL of *n*-pentane were added 1 g of K_2FeO_4 (5 mmol) and 2 g of K10 clay. The suspension was stirred at room temperature (see Table 8 for reaction times). The solid reagent was then filtered off with suction and washed with 5 × 20 mL of diethyl ether. The filtrates were combined, washed with 50 mL of water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on a silica gel column using benzene as eluent to yield pure acetophenone.

Oxidation of Hydrocarbons: General Procedure. Unless otherwise stated in Table 9, 2 g of K_2FeO_4 (10 mmol) and 4 g of K10 clay were suspended in 50 mL of a hydrocarbon substrate. A small amount of a linear alkane (0.3 g) was added as a GC internal standard, and the flask was hermetically stoppered. The reaction mixture was stirred in an oil bath at 75 °C. After 24, 48, and 72 h, the reaction mixture was allowed to cool down for a few minutes, and the supernatant solution was analyzed by GC. Yields were determined by the internal standard method and are based on the ferrate ions present.

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