Pergamon

0040-4039(95)01782-8

Oxidation of Organic Substrates with Potassium Ferrate (VI)
in the Presence of the K10 Montmorillonite

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Abstract Among various aluminosilicate supports. the K10 montmorillonite clay was the best catalyst for the oxidation of organic substrates with potassium ferrate (VI) Thus. a solid mixture of K_2FeO_4 and K10 has been used for the efficient oxidation of selected alcohols. benzylamine. thiophenol. and aniline in hydrocarbon solvents at room temperature Somewhat humid clay performs best, and it is important to control the amount of water associated to the solid support.

Potassium ferrate (VI) is a strong oxidizer isomorphous with K_2CrO_4 and K_2MnO_4.[1] Its use is attractive from an environmental standpoint, because unlike chromium[2,3] and manganese,[4] iron[5] is devoid of toxicity The oxidation of alcohols[6] and carbohydrates[7] by aqueous K_2FeO_4 has already been reported. Conversion of primary hydroxyl groups into aldehydes occurred with good yields and selectivity. However, it requires strongly basic aqueous media, incompatible with most organic substrates. In order to overcome the solubility problem, attempts have been made to use potassium ferrate in mixed solvents[8] or under phase-transfer catalysis conditions[9]. Under heterogeneous conditions, allylic, benzylic, and saturated secondary alcohols were efficiently oxidized to the corresponding carbonyl derivatives by a solid mixture of K_2FeO_4, Al_2O_3, and $CuSO_4.5\ H_2O$ in benzene.[10]

These promising earlier results prompted us to search an heterogeneous catalyst to promote oxidation of organic substrates by potassium ferrate in organic solvents. Encouraging indications that aluminosilicate minerals were promising candidates for such a goal came from another reagent developed in our laboratory under the nickname "Clayfen", for clay-supported ferric nitrate[11] Besides various other applications, "Clayfen" oxidizes a variety of secondary alcohols into aldehydes or ketones under mild reaction conditions.[12] Thus, replacing iron (III) with iron (VI) would, we surmised, boost the oxidizing properties of the solid reagent

To test the validity of our assumption, we have carried out oxidation of benzyl alcohol by potassium ferrate in the presence of a large number of aluminosilicate supports. The use of K10 montmorillonite, a cheap industrial acidic clay, resulted in quantitative conversion of benzyl alcohol into benzaldehyde within a few hours at room temperature, with no concomitant formation of benzoic acid. Acidic faujasite-type zeolites, such as the industrial ZF520 variety (Si/Al=20) or the ultra-stable Y zeolite (USY, Si/Al>100) were also efficient catalysts, although slightly less active than the montmorillonite clay. Thus, the reaction has been extended to a variety of other substrates using the K10 clay as a catalyst.

Potassium ferrate[13] is prepared by oxidizing ferric nitrate with sodium or potassium hypochlorite, followed by precipitation from concentrated aqueous potassium hydroxide.[14, 15] Its purity, as determined by the chromite method,[16] was higher than 94%. A typical oxidation procedure is: to 5 mmol of a substrate in 50 mL of n-pentane are added 2 g of K_2FeO_4 (10 mmol) and 4 g of K10 montmorillonite. The suspension is vigorously stirred at room temperature. After completion of the reaction, the solid reagent is filtered off with suction and washed with 3 x 20 mL of diethyl ether. The filtrates are gathered and evaporated under reduced pressure to afford the product.

The oxidation of various alcohols is summarized in Table 1. The reactions are usually complete within a few hours at room temperature. Only borneol which lacks any activation requires a longer reaction time. A single product is obtained in all cases, except with benzoin which undergoes an oxidative cleavage into benzaldehyde besides its oxidation into benzil. Although isolated yields are usually high, full recovery of benzaldehyde, furfuraldehyde, and 1,4-benzoquinone could not be 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 account for the loss of organic materials.

We tested on other functions than alcohols the generality of our reagent. At room temperature, benzylamine is converted by K_2FeO_4 - K10 into benzaldehyde (85% isolated yield after 3 hours). Under reflux conditions, the aldehyde reacts immediately with the remaining substrate so that the corresponding Schiff base, N-benzylbenzaldimine, is the main product isolated. The coupling of thiophenol into diphenyl disulfide is a convenient reactivity test for supported oxidizing reagents.[11] A mixture of K_2FeO_4 and K10 (2 g each) oxidizes thiophenol (5 mmol) dissolved in cyclohexane (50 mL), leading to an 88% isolated yield of the coupling product within 15 minutes. Coupling reactions of aromatic amines to their corresponding azo derivatives were also investigated using aniline as test-substrate. Azobenzene was formed in high yield but resisted crystallization.

The role of the K10 solid support is not fully understood at present but the humidity that it contains (about 12 weight %) has a considerable influence on the course of the reaction. Drying the clay catalyst overnight in a vacuum oven at 40°C under 1.5 mm Hg drastically reduces its activity, and a meager 9% yield of benzaldehyde is obtained after 24 h, whereas a quantitative conversion occurs within a few hours when the crude aluminosilicate is used under similar conditions (Table 2). In the absence of any catalyst, the reaction proceeds faster then in the presence of the dried clay, probably because the latter acts as a drying agent to remove any residual humidity

Table 1. Oxidation of alcohols (5 mmol) with K_2FeO_4 (2 g, 10 mmol) and K10 (4 g) at room temperature in
n-pentane (50 mL)

Substrate	Time, h	Conversion, %[a]	Product[b]	Isolated Yield, %
benzyl alcohol	3	100	benzaldehyde	63
furfuryl alcohol	4	94	furfuraldehyde	54
1-phenylethanol	2.5	100	acetophenone	98
benzhydrol	2	100	benzophenone	100
benzoin	2	100	benzil	36
cinnamyl alcohol	2	100	cinnamaldehyde	88
borneol	24	93	camphor	88
hydroquinone	0.5	100	1,4-benzoquinone	56

[a] monitored by GC or by TLC

[b] identified by comparison of their IR spectra and GC retention times with those of authentic samples

from the reaction medium. These results confirm previous observations by Menger and Lee on potassium permanganate oxidation in the presence of hydrated salts such as $CuSO_4.5 \, H_2O$. They were the first to stress the importance of water in solid-state oxidation, and they showed that carefully dried $KMnO_4$ failed to oxidize secondary alcohols into ketones.[1"] However, the clay does not serve only as a source of humidity in our system. A control experiment performed with a mixture of K_2FeO_4 and the amount of H_2O corresponding to 1 g of crude montmorillonite gave results intermediate between those obtained in the presence of dry and crude clays.

We made also the intriguing and promising observation that the cyclohexane solvent is not inert towards K_2FeO_4 in the presence of K10 clay and turns into significant amounts of cyclohexanol and cyclohexanone. For instance, stirring 2 g of K_2FeO_4 (10 mmol) and 4 g of K10 in 50 mL of cylohexane for 3 days at 75°C affords a 51/49 mixture of cyclohexanol/one with an overall 14% yield based on ferrate. This result clearly demonstrates the prowess of potassium ferrate as a strong oxidizer when used in conjunction with appropriate heterogeneous catalysts. Detailed examination of these systems is currently underway and will be reported in due course.

Table 2. Oxidation of benzyl alcohol (2 mmol) by K_2FeO_4 (1g, 5 mmol) in cyclohexane (30 mL) under various conditions (see text).

Catalyst	GC Yield, %		
	2 h reaction	8 h reaction	24 h reaction
none	1	14	44
dry K10 (1 g)	1	2	9
H_2O (0.13 g)	56	71	82
crude K10 (1 g)	84	99	100

Acknowledgments

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13. The first mention of this compound dates back to 1702, when the German physician and chemist Georg Stahl -one of the forerunners of the Chemical Revolution- reported obtaining an unstable solution of red purple color upon dissolving in water the molten residue from detonating a mixture of salpeter and iron filings (Stahl, G. E. *Opusculum Chymico-Physico-Medicum*, Halae-Magdegurgiae, 1715, p. 742). Similar colors, which we now know to be characteristic of the FeO_4^{2-} ferrate anion, were reported by Eckeberg (cited by Moeser, L., see below) and by Becquerel (Becquerel, A. *Ann. Chim. Phys.* **1834**, *51*, 105) in 1834, after mixes of potash and various iron ores were heated-up to the red. Frémy in the 1840s was the first to suggest formation of a high-valent iron derivative associated with this color, which he expressed with an FeO_3-type formula (Frémy, E. *Ann. Chim. Phys.* **1844**, *12 (Sér. 3)*, 361-382). By the time, Moeser published his comprehensive review in 1897 (Moeser, L. *J. prakt. Chem.* **1897**, *56*, 425-437), three preparative routes had been laid out: (i) the dry way pioneered by Stahl, Eckeberg, and Becquerel; (ii) electrolysis of a potassium hydroxide solution using an iron anode; (iii) the wet way, by oxidation of a basic solution of a ferric salt with hypochlorite or hypobromite. Only the latter has endured into the present time.

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