Photochemical Oxidation of Alcohols Using Ferric Chloride

Virgil I. Stenberg,* S. P. Singh, N. K. Narain, and S. S. Parmar

Departments of Chemistry and Physiology-Pharmacology, The University of North Dakota, Grand Forks, North Dakota 58202

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We wish to report quantitative measurements on the formation of aldehydes and ketones during the photochemical oxidation of alcohols by ferric chloride.[1] From the standpoint of organic chemistry, the quantitative information and the knowledge that primary alcohols do not form acids during the oxidation are useful. It is evident that the ferric ion in the excited state is a much stronger oxidizing agent than in the ground state. The emphasis of earlier studies[2–6] has been mainly on the ferric chloride participation, the quantum yields, the effect of acid, and the influence of excess chloride ion on the reaction. The irradiation of an ethanolic ferric chloride solution at 77 K yields the $CH_3\dot{C}HOH$ radical as observed by EPR spectra.[7,8] Methanolic and ethanolic solutions of ferric perchlorate also show the same oxidation–reduction phenomena when irradiated at 365 nm.[5,9,10] Ketyl radicals are also found in these irradiation solutions.

The oxidation of primary and secondary alcohols to the corresponding aldehydes or ketones was achieved by irradiation in a Rayonet photochemical reactor for 5–10 h using the 350-nm lamps in a nitrogen atmosphere. The presence of ferric chloride (0.15 M) was found to be essential for the photochemical oxidation. The isolation and characterization of dimedone and 2,4-dinitrophenylhydrazone derivatives established the formation of the aldehydes and ketones. This was confirmed by comparing the retention times of the aldehydes and ketones on GLC and comparing them with those of the authentic samples. The completion of the reaction was marked by the disappearance of the yellow color of ferric chloride, a positive test for the ferrous ion in the irradiated solutions, and the formation of an intense blue precipitate (Turnbull's blue) with potassium hexacyanoferrate(III). The concentrations of the aldehydes and ketones formed were determined by GLC and their percentages are reported in Table I. The reaction mixtures with primary alcohols were devoid of the corresponding acids indicating that the reaction proceeded only up to the aldehyde stage. The reactions were unsuccessful in the presence of air.

From the data of Table I, several generalizations can be made. The yields decrease with increasing chain length for both primary and secondary alcohols, and secondary alcohols are more dependent on chain length than are the primary ones. A suggested reason for this behavior is that, for the longer chain length compounds, there are competing radical–hydrocarbon reactions which occur at the expense of the alcohol reaction.

Table I. Photochemical Oxidation[a] of Aliphatic Alcohols in Presence of Ferric Chloride

Alcohol	Registry no.	Irradiation time, h	2,4-DNP mp, °C	Registry no.	Dimedone, mp, °C	Registry no.	Yield, %[b]
Methanol[c]	67-56-1	5	161	1081-15-8	185	2181-22-8	
Ethanol	64-17-5	5	144	1019-57-4	140	3316-11-8	86.8
1-Propanol	71-23-8	5	152	725-00-8	151	19419-21-7	52.5
2-Methylpropanol	78-83-1	5	186–188	2057-82-1	150	3316-12-9	70.5
1-Butanol	71-36-3	5	119	1527-98-6	140	19419-22-8	60
2-Propanol	67-63-0	10	126	1567-89-1			100
2-Butanol	78-92-2	10	112–113	958-60-1			74.5
2-Pentanol	6032-29-7	10	141	1636-82-4			45.2
2-Hexanol	626-93-7	10	105	2348-17-6			35.5

[a] Photochemical oxidation was carried out under nitrogen atmosphere. The Rayonet photochemical reactor equipped with 350-nm lamps was used. [b] Represents yields of the respective aldehyde or ketone formed during photochemical oxidation. [c] Owing to difficulty in preparing the formaldehyde solution, the percentage yield of formaldehyde could not be determined accurately.

Experimental Section

All melting points were taken on a Fisher-Johns melting point apparatus and are corrected. All the alcohols and their corresponding aldehydes/ketones were purchased from Aldrich Chemical Co., Milwaukee, Wis. Anhydrous, sublimed ferric chloride was purchased from Fisher Scientific Co., Fair Lawn, N.J. Alcohols and carbonyl compounds were distilled and their purity was checked by GLC.

Irradiation of Alcohols. The irradiations were carried out in a Rayonet photochemical reactor using 350-nm lamps under a nitrogen atmosphere. Ferric chloride (0.15 M) was dissolved in 20 ml of an appropriate alcohol and the solution was placed in a Pyrex vessel. The irradiation was stopped when the reaction solution became colorless. The photochemical reduction of ferric ion into ferrous ion was substantiated by the formation of a characteristic blue precipitate (Turnbull's blue) by adding potassium hexacyanoferrate(III) to a portion of the irradiated solution.

The 2,4-dinitrophenylhydrazone and dimedone derivatives of aldehyde and ketone products were prepared from the reaction solution by usual methods[11] after removing ferric chloride. The melting points of these derivatives are recorded in Table I. The GLC analyses were performed on a Varian Aerograph Model 90-P instrument equipped with a 20 m × 4 mm column containing 20% Carbowax on 60/80 Chromosorb W.

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Registry No.—Ferric chloride, 7705-08-0.

References and Notes

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