

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION-METAL COMPLEXES.

XVI.* AIR OXIDATION OF ALKYLAROMATIC AND SATURATED HYDROCARBONS SENSITIZED BY UO_2^{2+}

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Uranyl ion UO_2^{2+} is known to be a good sensitizer for air oxidation of several organic compounds: olefins, alcohols, phenols, and amines. The process may begin with extraction of a H atom from the organic substrate by UO_2^{2+} [2-6].

In the present work, we report the first results of using UO_2^{2+} as a sensitizer for solution oxidation of alkylaromatic and saturated hydrocarbons by air. Irradiation with an unfiltered high-pressure mercury lamp in a glass cylinder ($\lambda > 320$ nm) of a solution of toluene and UO_2Cl_2 in CH_3COOH produces benzaldehyde as the main product. The UO_2^{2+} concentration decreases. The kinetics of benzaldehyde production and UO_2^{2+} consumption are illustrated in Fig. 1. In the absence of toluene, UO_2^{2+} is not reduced. It should be noted that benzaldehyde is not produced if the reaction is conducted under argon.

The initial rate of benzaldehyde production at large UO_2^{2+} concentrations depends on the sensitizer concentration.

Initial UO_2^{2+} concentration, $c \cdot 10^3$, M	0.8	1.7	8.5	17.0
C_6H_5CHO concentration after 1 h irradiation, $c \cdot 10^3$, M	1.3	2.0	4.7	2.0

Oxidation of cyclohexane (0.53 M) in CH_3COOH in the presence of $1.7 \cdot 10^{-3}$ M UO_2Cl_2 produces cyclohexanone and cyclohexanol.

Irradiation time, h	0.7	1.0	2.5
Cyclohexanone concentration, $c \cdot 10^3$, M	5.8	7.8	11.7
Cyclohexanol concentration, $c \cdot 10^3$, M	2.8	4.3	7.0

We also found that oxidation of alkylarenes and alkanes sensitized by UO_2^{2+} can be carried out in CH_3CN . The rate of production is about the same as in CH_3COOH . Irradiation of a solution of UO_2Cl_2 ($1.7 \cdot 10^{-3}$ M) saturated with an atmosphere of methane in CH_3CN produces formaldehyde ($8.3 \cdot 10^{-5}$ M) after 3.5 h irradiation. Finally, irradiation of a solution of ethylbenzene (0.87 M) in CH_3CN in the presence of the uranyl complex of meso-tetra(p-methoxyphenyl)porphine (L), LUO_2Cl_2 ($0.17 \cdot 10^{-3}$ M), produces acetophenone.

Irradiation time, h	1	2	3	5	6
$PhCOCH_3$ concentration, $c \cdot 10^3$, M	1.8	3.2	4.5	5.7	5.7

It can be proposed on the basis of the experimental data that the oxidation of hydrocarbons sensitized by UO_2^{2+} occurs as follows. A photoexcited sensitizer molecule extracts a H atom from the hydrocarbon substrate (the complex $ArH \cdot UO_2^{2+}$ may be formed for alkylarenes ArH [7], resulting in electron transfer from arene to U(VI)). The hydrocarbon radical formed reacts with O_2 to form a peroxide which decomposes to a stable product containing oxygen. The reduced U(V) species can be reoxidized by O_2 or the peroxide.

*For communication XV, see [1].

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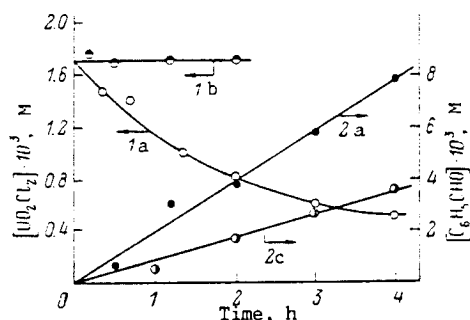


Fig. 1. Kinetics of UO_2Cl_2 consumption (1) and benzaldehyde production (2) during oxidation of toluene (0.87 M) by air in CH_3COOH . a, b) Initial UO_2^{2+} concentration $1.7 \cdot 10^{-3}$ M; b) without toluene; c) initial UO_2^{2+} concentration $0.17 \cdot 10^{-3}$ M.

EXPERIMENTAL

The concentration of oxidation products of toluene and ethylbenzene were determined spectrophotometrically on a Specord UV-Vis spectrophotometer using the absorption at λ 283 (benzaldehyde) and 278 nm (acetophenone). The concentrations of cyclohexanol and cyclohexanone were determined by GLC on a LKhM-80 chromatograph (0.25-0.315 mm Inerton AW-HMDS support coated with 5% Carbowax 1500, column length 2 m, argon carrier gas).

The reactions were carried out in a glass cylinder cooled with a water jacket (15°C). The mixtures were stirred vigorously using a magnetic stirrer. A high-pressure mercury lamp (1000 W) was used. The CH_3COOH reaction mixture was diluted with water and extracted with CHCl_3 . Benzaldehyde and acetophenone were isolated by TLC on Silufol UV-254 plates using hexane- CHCl_3 (5:2) eluent. The formaldehyde concentration was determined spectrophotometrically using absorption at λ 570 nm after reaction with a solution of chromotropic acid.

CONCLUSIONS

Irradiation of solutions of alkylarenes and alkanes in the presence of UO_2^{2+} in air produces oxidation products containing oxygen.

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