HYDROGEN PEROXIDE OXIDATION OF HYDROCARBONS CATALYZED BY Cr(VI) OXO COMPOUNDS

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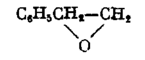
CrO_3, $(NBu_4)_2CrO_4$, $(NBu_4)_2Cr_2O_7$, and $(NBu_4)Cr_4O_{13}$ catalyze the hydrogen peroxide oxidation of cyclohexane, ethylbenzene, and styrene in acetonitrile. The active species is apparently a Cr(VI) peroxo complex.

Complexes of transition metals [1] and, in particular, chromium oxo compounds [2-7] catalyze the peroxide oxidation of alcohols, alkylaromatic hydrocarbons, and saturated hydrocarbons. In a continuation of a study of the oxidation of hydrocarbons catalyzed by Cr(VI) oxo compounds [8], we used hydrogen peroxide as the oxidizing agent. All the reactions were carried out in acetonitrile solution. Cyclohexane, ethylbenzene, and styrene served as the substrates, while various Cr(VI) oxo compounds, namely, CrO_3 (I), $(NBu_4)_2CrO_4$ (II), $(NBu_4)_2\cdot Cr_2O_7$ (III), and $(NBu_4)_2Cr_4O_{13}$ (IV), were used as the catalysts. The results are given in Table 1. The rate of the oxidation of cyclohexane or ethylbenzene is greatest when (III) is used as the catalyst. The accumulation of the products in the oxidation of ethylbenzene is complete after 24 h. The initial rate of benzaldehyde formation in the oxidation of styrene is greatest in the case of (III) but the maximum yield over seven days is obtained when (IV) is used. The kinetic curves for the products in the case of cyclohexane reach a plateau only after seven days. Catalyst (II) proved the least active in the oxidation of all three hydrocarbons studied.

In contrast to iodosobenzene oxidation catalyzed by CrO_3 [8], in which the Cr=O oxo fragment is the oxidizing species, a Cr(VI) peroxo complex formed from H_2O_2 and the Cr(VI) oxo compound is apparently the active species in the reaction with hydrogen peroxide.

TABLE 1. Hydrogen Peroxide Oxidation of Hydrocarbons Catalyzed by Cr(VI) Compounds*

Catalyst	Time, days	Oxidation products ($\times 10^5$, moles)						
		cyclohexane		ethylbenzene		styrene		
		$C_6H_{11}OH$	$C_6H_{10}O$	$C_6H_5CH\cdot(OH)CH_3$	$C_6H_5COCH_3$	C_6H_5CHO	$C_6H_5COCH_3$	 $\underset{\diagdown O \diagup}{C_6H_5CH_2{-}CH_2}$
(I)	1	1,8	1,5	1,3	2,0	16.0	0,2	0,1
	7	5,0	10,0	2,8	4,7	16,0	1.0	0,1
(II)	1	0,7	0,4	0,1	0,2	3.0	0,1	0,1
	7	1.1	0,7			28,2	0,2	0,8
(III)	1	4,7	5,3	2,5	4,8	25.0	1,0	1,6
	7	6,8	9,0			25.0	1.2	2,0
(IV)	1	3.7	2,7	1,9	3,2	20.0	0,4	0,4
	7	5,6	9,5			42.0	1,2	3,0

*Initial concentrations: 0.46 mole/liter hydrocarbon, $8.8\cdot10^{-2}$ mole/liter H_2O_2, and $5.0\cdot10^{-4}$ mole/liter catalyst. The reactions were carried out in acetonitrile at 20°C.

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The catalysts were prepared according to reported procedures [9, 10]. All the reactions were carried out in vessels protected from atmospheric moisture and light at 20°C. The total volume of the acetonitrile solutions was 10 ml. A sample of 0.1 ml 30% aq. H_2O_2 was used as the oxidizing agent. The oxidation products were analyzed by gas-liquid chromatography on an LKhM-80-6 chromatograph using a 2-m column packed with 5% Carbowax 1500 on 0.2-0.315 mm AW-HMDS Inerton with argon as the carrier gas.

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PHOTOOXIDATION OF CYCLOHEXANE BY $(Bu_4N)_2Cr_4O_{13}$ IN ACETONITRILE OR CH_2Cl_2

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Upon irradiation using light with $\lambda > 520$ nm, $(Bu_4N)_2Cr_4O_{13}$ oxidizes cyclohexane to cyclohexanol as the major product and cyclohexanone in acetonitrile and to cyclohexanol as the major product, cyclohexanone, and cyclohexyl chloride in CH_2Cl_2. Carrying out this reaction in the presence of air leads to a sharp increase in the yield of cyclohexanone.

Cr(VI) oxo compounds oxidize alkanes to oxygen-containing products [1, 2]. Thus, cyclohexane is oxidized by Cr(VI) compounds in acetic acid in the air upon irradiation to give adipic acid as the major product [3].

In the present work, we studied the photooxidation of cyclohexane in aprotic solvents, namely, acetonitrile and CH_2Cl_2. The oxidation of cyclohexane by $(Bu_4N)_2Cr_4O_{13}$ in acetonitrile in an argon atmosphere leads to the formation of mainly cyclohexanol with a relatively small amount of cyclohexanone (Fig. 1). The analogous reaction in CH_2Cl_2 also gives cyclohexanol as the major product with small amounts of cyclohexanone and cyclohexyl chloride (Fig. 2).

The amount of cyclohexanol is virtually unchanged when the photooxidation is carried out in the air but the yield of cyclohexanone is sharply increased (Fig. 1).

These results may be interpreted as follows. The reaction of hydrocarbon RH with the photoexcited Cr(VI) oxo compound leads to the abstraction of a hydrogen atom from the alkane and formation of a Cr(V) hydroxy derivative. The resultant radical $R^{\cdot}$ may abstract an OH group from the Cr(V) derivatives to form cyclohexanol or a chlorine atom from CH_2Cl_2 to form

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