

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), $(NBu_4)_2Cr_2O_7$ (III), and $(NBu_4)Cr_4O_{13}$ (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 iodobenzene 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		
		$C_6H_{11}OH$	$C_6H_{10}O$	$C_6H_5CH_2(OH)CH_3$	$C_6H_5COCH_3$	C_6H_5CHO	$C_6H_5COCH_3$	$C_6H_5CH=CH_2$
(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, $8.8 \cdot 10^{-2}$ mole/liter H_2O_2 , and $5.0 \cdot 10^{-4}$ mole/liter catalyst. The reactions were carried out in acetonitrile at 20°C.

EXPERIMENTAL

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. H₂O₂ 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.

LITERATURE CITED

1. G. B. Shul'pin, *Organic Reactions Catalyzed by Transition Metal Complexes* [in Russian], Nauka, Moscow (1988).
2. J. Muzart, *Tetrahedron Lett.*, **27**, 3139 (1986).
3. J. Muzart, *Tetrahedron Lett.*, **28**, 2131 (1987).
4. J. Muzart, *Tetrahedron Lett.*, **28**, 2133 (1987).
5. J. Muzart, *New. J. Chem.*, **13**, 9 (1989).
6. S. Kanemoto, S. Matsubara, K. Takai, et al., *Bull. Chem. Soc. Jpn.*, **61**, 3607 (1988).
7. E. Daire, H. Mimoun, and L. Saussine, *Nouv. J. Chim.*, **8**, No. 5, 271 (1984).
8. G. B. Shul'pin and A. N. Druzhinina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 1185 (1989).
9. E. Santaniello and P. Ferraboschi, *Synth. Commun.*, **10**, 75 (1980).
10. E. Shill, in: *Inorganic Synthesis Handbook* [Russian translation], G. Brauer (ed.), Mir, Moscow (1986), p. 1891.