

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION-METAL COMPLEXES.

X. OXIDATION OF ALKANES AND ALKYL BENZENES BY Cr(VI) OXO COMPOUNDS ON EXPOSURE TO LIGHT*

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Processes where a C-H bond in saturated and aromatic compounds is activated by metal complexes have been intensively studied recently [3-9] and may be divided into two groups depending on the character of the complex. The most numerous are reactions in which the metal complex acts as a nucleophile (see review [3] and recent articles [10, 11]). The components of the C-H bond oxidatively add to the coordinately unsaturated part of the complex, forming an alkylhydride or arylhydride (i.e., an organometallic [12]) derivative. Reactions of the first type usually involve complexes of metals in low oxidation states and hydrides. Very few examples are known of reactions of the second type, where the attacking metal-containing species is an electrophile. The interaction of the $PtCl_6^{2-}$ ion with arenes has been studied in most detail [13-15]. This reaction is also stimulated by the action of light [15-17] or γ radiation [18]. The porphyrin complex of Rh(III) [19], chloride derivatives of Au(III) [20, 21], and Pd(II) compounds [22] metallate arenes in a similar manner. In all cases the C-H bond interacts directly with the metal ion to form compounds which contain a metal-carbon bond. It should be noted that in certain cases complexes of metals in a high oxidation state metallate arenes according to a mechanism which is not that of electrophilic substitution [23, 24]. Examples are also known of activation (usually photochemical) of a C-H bond by metal complexes that apparently occurs with formation of radical species [1, 25-27]. The electrophilic species incorporating a metal ion in a high oxidation state may also react with a C-H bond without direct contact with the metal, interaction taking place through the ligand. Oxygen in oxo compounds (of manganese, chromium, and other metals) is one such ligand. The special interest in these processes is connected with the relatively recent discovery of the decisive role of the ferryl Fe=O fragment in activation of a C-H bond by the natural enzyme cytochrome P-450 [3, 28, 29]. Iron, manganese, and chromium porphyrin complexes are close models of the natural catalyst [3, 30-35]. It is interesting that oxidation of hydrocarbons in the presence of metalloporphyrins may be stimulated by the action of light [36, 37]. Catalysis by complexes which model oxidation-reduction enzymes is important in organic synthesis [38]. Transition-metal oxo compounds, which are well known and widely used in organic chemistry, may be considered in certain aspects as models for enzymes [3]. It is known, in fact, that oxidation of arenes by chromium(VI) compounds is associated with the so-called NIH shift typical of biological oxidation processes [39].

This investigation is concerned with photochemical oxidation of hydrocarbons by Cr(VI) oxo compounds. Such a process occurring in the absence of light is well known and widely used in organic synthesis [40]. On the other hand, photoactivity of Cr(VI) oxo compounds has been observed in the oxidation of alcohols and certain other compounds [41-44] and the oxidation of derivatives of 1,3,3-trimethylnorbornane by chromyl acetate is accelerated by the action of UV light [45]. The oxidation of hydrocarbons is quite slow at room temperature in the dark. Exposure of a hydrocarbon to UV light in an oxygen atmosphere in the absence of metal compounds induces oxidation, which proceeds at a very low rate [46]. Photochemical oxidation of alkanes has been successful in the presence of mercury or its salts [47, 48].

In this work we used $Cr_2O_7^{2-}$ and CrO_4^{2-} ions [49] or CrO_3 as oxidizing agents. The substrates were benzene, toluene, ethylbenzene, cyclohexane, and adamantane. Oxidation was carried out in a homogeneous solution of CrO_3 in CH_3COOH or in a two-phase system of the hydrocarbon and an aqueous solution of K_2CrO_4 in conditions of interphase catalysis [50].

*For communication IX, see [1]; for preliminary communication, see [2].

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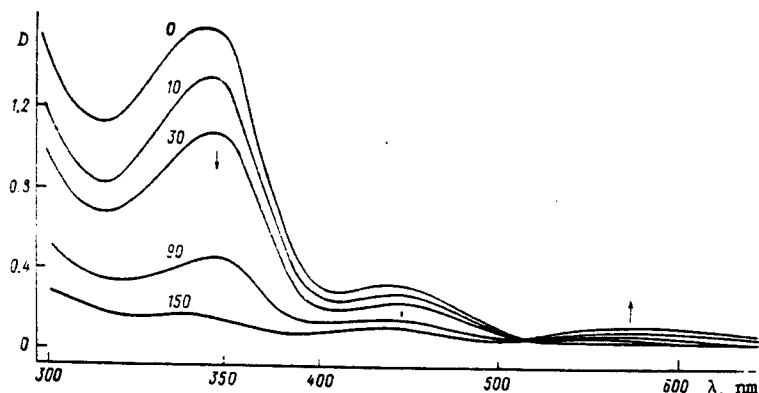


Fig. 1. Change with time of the electronic absorption spectrum of a solution of CrO_3 ($2.5 \cdot 10^{-3}$ M) and benzene (1.44 M) in a $\text{CH}_3\text{COOH-H}_2\text{O}$ (4:1) mixture during exposure. Exposure time (min) is indicated above the corresponding curves.

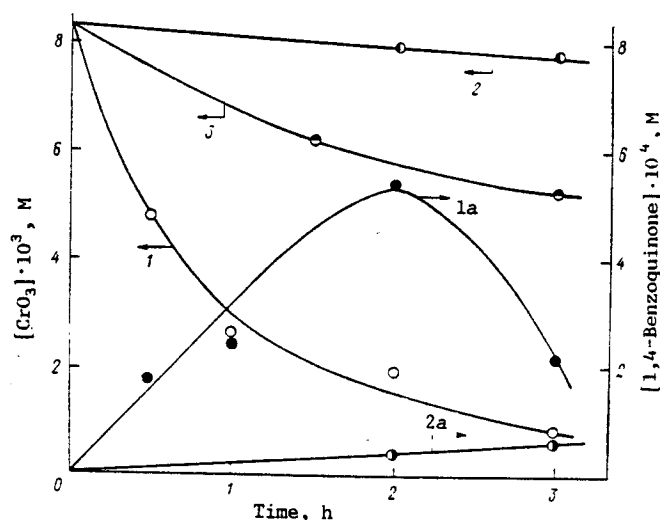


Fig. 2. Kinetic curves for CrO_3 consumption (initial concentration $8.3 \cdot 10^{-3}$ M) and 1,4-benzoquinone accumulation during oxidation of benzene (1.9 M) in CH_3COOH . 1) Consumption of CrO_3 during exposure; 1a) accumulation of 1,4-benzoquinone in the same reaction; 2) consumption of CrO_3 in the dark; 2a) accumulation of 1,4-benzoquinone in the same reaction; 3) consumption of CrO_3 during exposure in the absence of benzene.

Exposure of a solution of CrO_3 and benzene in aqueous acetic acid to the total light from a high-pressure mercury lamp (500 W) leads to a gradual decrease in the electronic spectrum of the intensity of the absorption bands with $\lambda \sim 350$ and 450 nm, corresponding to the Cr(VI) compounds, and a simultaneous increase in absorption ($\lambda_{\text{max}} \sim 580$ nm) of the corresponding Cr(III) derivative (Fig. 1). The reduction of Cr(VI) to Cr(III) is accompanied by formation of quinone, the amount of which was determined by liquid chromatography. Figure 2 shows kinetic curves for CrO_3 consumption and quinone accumulation when the photochemical reaction was carried out in anhydrous acetic acid. Reduction of Cr(VI) also occurs on exposure in the absence of benzene, acetic acid then acting as the reducing agent in a much slower reaction. Reaction is extremely slow in the dark even in the presence of benzene. The maximum concentration of quinone in solution is observed 2 h after the start of exposure (18% yield calculated with respect to Cr), and then its level decreases. Evidently the quinone undergoes further oxidative changes.

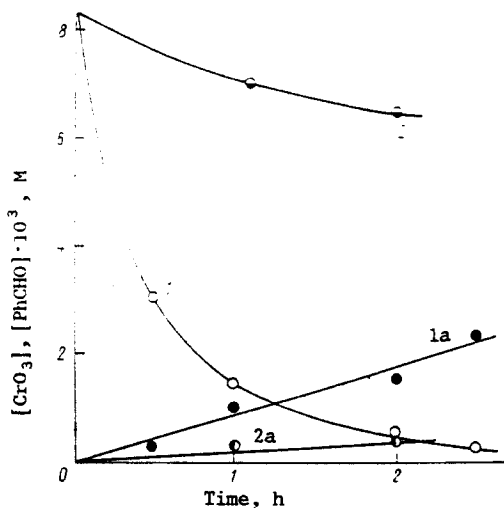


Fig. 3

Fig. 3. Kinetic curves for CrO_3 consumption (initial concentration $8.3 \cdot 10^{-3}$ M) and benzaldehyde accumulation during oxidation of toluene (1.7 M) in CH_3COOH . 1) Consumption of CrO_3 during exposure; 1a) accumulation of benzaldehyde in the same reaction; 2) consumption of CrO_3 in the dark; 2a) accumulation of benzaldehyde in the same reaction.

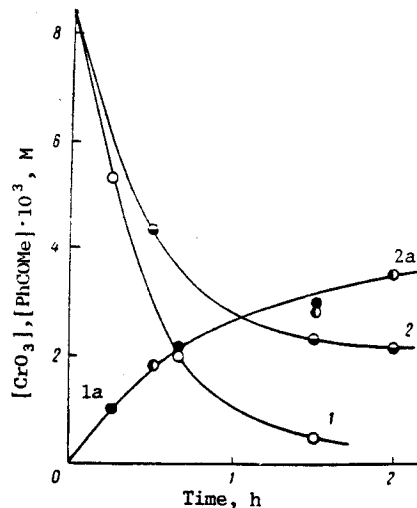


Fig. 4

Fig. 4. Kinetic curves for CrO_3 consumption (initial concentration $8.3 \cdot 10^{-3}$ M) and acetophenone accumulation during oxidation of ethylbenzene (1.6 M) in CH_3COOH . 1) Consumption of CrO_3 during exposure; 1a) accumulation of acetophenone in the same reaction; 2) consumption of CrO_3 in the dark; 2) accumulation of acetophenone in the same reaction.

TABLE 1. Oxidation of Substituted Toluenes by Cr(VI) Oxo Compounds

Substrate	Method ^a	Time, h	Products isolated [% yield calc. w. resp. to Cr(VI)]
p- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$	a	2	p- $\text{CH}_3\text{C}_6\text{H}_4\text{COOH}$ (20)
	b	2	p- $\text{CH}_3\text{C}_6\text{H}_4\text{COOH}$ (30)
	c	6	p- $\text{CH}_3\text{C}_6\text{H}_4\text{CHO}$ (36)
m- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$	a	2	m- $\text{CH}_3\text{C}_6\text{H}_4\text{COOH}$ (6)
	b	3.5	m- $\text{CH}_3\text{C}_6\text{H}_4\text{COOH}$ (30)
m- $\text{ClC}_6\text{H}_4\text{CH}_3$	b	6	m- $\text{ClC}_6\text{H}_4\text{CHO}$ (16)
	c	4	m- $\text{ClC}_6\text{H}_4\text{CHO}$ (85)
	a	5	p- $\text{BrC}_6\text{H}_4\text{CHO}$ (5)
p- $\text{BrC}_6\text{H}_4\text{CH}_3$	a	5	p- $\text{BrC}_6\text{H}_4\text{COOH}$ (15)
	b	5	p- $\text{BrC}_6\text{H}_4\text{CHO}$ (16)
p- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_3$	a	5	p- $\text{BrC}_6\text{H}_4\text{COOH}$ (10)
	c	2	p- $\text{CH}_3\text{OC}_6\text{H}_4\text{CHO}$ (43)

Note. a) See Experimental.

Toluene and ethylbenzene are oxidized much faster than benzene. The products formed are benzaldehyde and acetophenone, respectively (Figs. 3 and 4). Light has an appreciable accelerating effect in the case of toluene. Ethylbenzene is rapidly oxidized even in the dark, so that light scarcely affects the reaction rate in homogeneous solution.

When a solution of 10^{-4} mole CrO_3 and 2 ml cyclohexane in 10 ml acetic acid is exposed for 75 min, 10^{-5} mole of adipic acid (33% yield calculated with respect to Cr) is formed (detected by liquid chromatography). The mixture also contained other unidentified products (five peaks on the chromatogram).

A study was also made of the effects of initial concentration of substrate and light intensity on the rate of oxidation of cyclohexane in homogeneous solution. Thus, it appeared that for $[\text{CrO}_3]_0 = 2.9 \cdot 10^{-3}$ M the CrO_3 concentration falls in the first 10 min of exposure

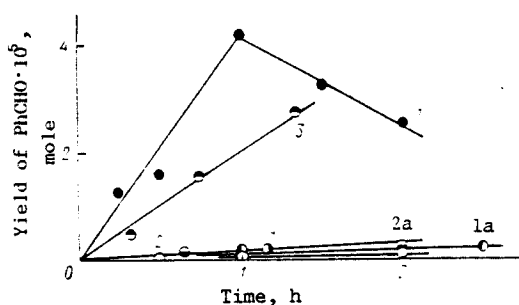


Fig. 5

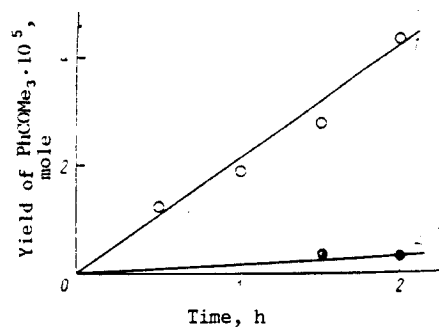


Fig. 6

Fig. 5. Kinetic curves for accumulation of benzaldehyde during oxidation of toluene (2 ml) in an emulsion (10 ml H₂O, 0.05 g Bu₄NBr). 1) 10⁻⁴ mole K₂CrO₄ oxidizing agent, 0.1 ml H₂SO₄, exposure; 1a) the same, in the dark; 2) 10⁻⁴ mole K₂CrO₄ oxidizing agent, exposure; 2a) the same, in the dark; 3) 5 · 10⁻⁵ mole K₂Cr₂O₇ oxidizing agent, 0.05 ml H₂SO₄, exposure; 4) 5 · 10⁻⁵ mole K₂Cr₂O₇ oxidizing agent, exposure.

Fig. 6. Kinetic curves for accumulation of acetophenone during oxidation of ethylbenzene (2 ml) by K₂Cr₂O₇ (5 · 10⁻⁵ mole) in an emulsion (10 ml H₂O, 0.05 g Bu₄NBr, 0.05 ml H₂SO₄) during exposure (1) and in the dark (2).

at a faster rate than the cyclohexane concentration increases (α is the percentage drop in CrO₃ concentration).

[Cyclohexane] ₀ , M	0	0.15	1.5	3.0
α , %	50	52	53	67

It is evident that this reaction involves quite intensive oxidation of acetic acid as well as cyclohexane. Using light-absorbing metallic gratings it was possible to determine the effect of the intensity of incident light I on the reaction rate (the intensity of the total light from the lamp without use of a grating was taken as 100%). Thus, the value of α for a solution with [CrO₃]₀ = 2.9 · 10⁻³ M and a cyclohexane concentration of 1.5 M is:

I, %	100	50	18	7	0
α , %	53	29	24	15	14

Photooxidation of adamantane in homogeneous solution in CH₃COOH leads to formation of 1-adamantanol and adamantanone (determined by GLC) in a ratio of -7:1. Without exposure the reaction is slower. Thus, exposure for 5 h of a solution of 10⁻⁴ mole CrO₃ in 10 ml CH₃COOH with 0.2 g adamantane in suspension forms a total yield of oxidation products of 6.5% calculated with respect to the chromium compound, whereas the yield over the same period in the dark is only 0.8%.

The accelerating effect of light on hydrocarbon oxidation is especially pronounced in a two-phase system, where the organic substrate and the aqueous solution of CrO₄²⁻ ion are not mixed. The salt Bu₄NBr was used as an interphase carrier. It appeared that reaction occurred only in acid solution (on addition of H₂SO₄) (Figs. 5 and 6). The amount of benzaldehyde formed reaches a maximum 1 h after the start of exposure (56% yield with respect to Cr). In acid solution with an oxidizing agent present, benzaldehyde probably undergoes further changes by the action of light. The organic solvent used during oxidation of adamantane in a two-phase system was 1,2-dichloroethane. Oxidation by K₂Cr₂O₇ in the presence of Bu₄NBr and H₂SO₄ gives a mixture of 1-adamantanol and adamantanone with a total yield of 52% during exposure and only 19% in the dark.

The suitability of this method for synthesis was examined in a study of photooxidation of some substituted toluenes. The results obtained are shown in Table 1. Oxidation by CrO₃ in aqueous acetic acid in the dark at 70°C (method a) leads mainly to formation of the corresponding benzoic acids in relatively low yield. Exposure of a solution of a substituted toluene and CrO₃ in CH₃COOH-H₂O at 7°C (method b) gives both a substituted benzoic acid and a substituted benzaldehyde. The yields of oxidation products isolated are not high. Finally, oxidation by potassium bichromate in a two-phase system with exposure (method c) leads to formation mainly of substituted aldehydes with good yields.

EXPERIMENTAL

Reaction products were determined quantitatively by liquid chromatography using a Laboratorni pristroje type 800 apparatus, Separon SIX C 18 carrier, and 4.5:1 methanol-water eluant; adipic acid was identified by refractive index and aromatic compounds by their UV-absorption spectra. The adamantane oxidation products, and benzaldehyde in certain experiments, were analyzed by GLC using a Chrom-4 chromatograph (1200 × 3 mm column; carrier GAS Chrom-R; 80/100 mesh + Carbowax 20 M or, in the case of benzaldehyde, Inerton + 5% Carbowax 20 M, 100°C).

All reactions were conducted in air in a cylindrical glass vessel enclosed in a cooling water jacket with vigorous magnetic stirring and intense exposure. High-pressure mercury lamps were used as light sources (500 W in the kinetic experiments and 1000 W for oxidation of the substituted toluenes). All the kinetic experiments were performed at 200°C. The concentration of Cr(VI) compounds was determined spectrophotometrically from absorption in the visible region using a Unicam P 800B. The amount of oxidation product formed was determined as follows: After exposure for a known time, the solution was diluted twofold with water and extracted with chloroform (3 × 10 ml), and the chloroform solution was washed with water, NaHCO₃ solution, and water and dried with Na₂SO₄; the chloroform was evaporated under reduced pressure, and the amount of oxidation product determined chromatographically.

Oxidation of Substituted Toluenes. a. A solution of 0.1 g CrO₃ and a tenfold excess of organic substrate in 10 ml 10:1 CH₃COOH-H₂O mixture was kept in the dark at 70°C (reaction time is shown in Table 1). Water (10 ml) was added to the solution, followed by extraction with chloroform (3 × 20 ml); the extract was washed with water, NaHCO₃ solution, water, and dried with Na₂SO₄. The chloroform was evaporated under reduced pressure and the residue chromatographed on silica gel plates (5:1 hexane-acetone eluant).

b. A solution of 0.05 g CrO₃ and a tenfold excess of organic substrate in 20 ml 40:1 CH₃COOH-H₂O mixture in a glass vessel, cooled to 7°C with a water jacket, was exposed with vigorous stirring to the total light of a DRS-1000 high-pressure mercury lamp (1000 W). The products isolated are described above.

c. A solution of 0.059 g K₂Cr₂O₇, 0.2 ml conc. H₂SO₄, and 0.1 g Bu₄NBr in 25 ml water with 2 ml organic substrate was exposed in a cylindrical vessel with vigorous stirring and cooling down to 10°C. The products isolated are described above.

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CONCLUSIONS

Exposure to light significantly accelerates oxidation of hydrocarbons by Cr(VI) oxo compounds, the reaction being conducted in homogeneous solution in CH₃COOH or in a two-phase system in the presence of a catalyst of interphase transport.

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