

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION-METAL COMPLEXES.

XI. RELATIVE RATES OF OXIDATION OF THE METHYL GROUP IN SUBSTITUTED TOLUENES BY Cr(VI) OXO COMPOUNDS IN THERMAL AND PHOTOCHEMICAL REACTIONS*

G. B. Shul'pin and A. N. Kitaigorodskii

UDC 541.145:542.943.7:

547.53

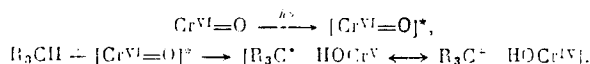
In previous work we have investigated certain features of the photochemical oxidation of aromatic and alkylaromatic compounds by Cr(VI) oxo compounds [1, 2]. It would be of interest to ascertain if the mechanism of the photochemical process differs from that of the thermal process. One of the criteria for similarity or difference in the mechanisms would appear in determination of the relative rates of oxidation of the methyl group in various substituted toluenes.

Other authors [3, 4] have determined the rates of thermal oxidation of solutions of substituted toluenes and diphenylmethane derivatives in acetic acid using chromic anhydride. They found that electron-acceptor groups in the toluene ring lower the reaction rate, the rate decreasing in the following sequence: H > p-Br > p-Cl > p-CN > p-NO₂ [3]. The logarithmic rates of oxidation of substituted diphenylmethanes correlate with the Brown σ^+ constants, the value of ρ^+ being equal to -1.17 [4].

We have used the competing-reaction method to study the relative rates of oxidation of the methyl group in substituted toluenes in both thermal and photochemical reactions. A mixture of two substituted toluenes in 1:1 ratio was used in excess with respect to the Cr(VI) oxo compound. Reaction was stopped in the initial stage: after 8-45 min in the thermal reaction at 70°C and after 20-270 min in the photochemical reaction at 7°C. The mixture of the two resulting substituted benzaldehydes (the mixture contains only insignificant amounts of benzoic acids) was isolated by TLC and the proportions of the aldehydes determined by PMR. The results obtained are shown in Table 1.

In homogeneous solution in CH₃COOH, for both thermal and photochemical reactions, electron-donor substituents slightly accelerate the reaction and electron-acceptor substituents inhibit the process. The sharp increase in rate when X = p-OCH₃ attracts attention. Omitting the data for this substituent, the logarithmic relative rates of thermal and photochemical reactions in homogeneous conditions correlate with the Brown σ^+ constants (see Fig. 1). The value of ρ^+ is -1.5, in good agreement with the data obtained for oxidation of substituted diphenylmethanes (see above) [13]. It is interesting to note that an anomalously high rate for X = p-OCH₃ was also observed in thermal oxidation of diphenylmethanes. According to preliminary data (see Table 1), the dependence of the logarithmic rates of oxidation on σ^+ in the case of reaction in a two-phase system with an interphase carrier is different from that of the process in homogeneous solution. This is perhaps connected with the different solubility of the Cr(VI) compounds in the organic substrates.

Thus, the agreement between the values of ρ^+ for thermal and photochemical oxidation of substituted toluenes in homogeneous solution in CH₃COOH suggests that the light-stimulated reaction follows the same mechanism as the thermal process [5, 6]. Interaction of an electronically excited Cr(VI) species with a C-H bond leads to abstraction of a hydrogen atom and formation of a pair, conventionally represented in the form of a superposition of two structures, one radical and the other ionic:



Aldehydes or ketones are eventually produced from the resulting radicals or carbonium ions.

*For communication X, see [1].

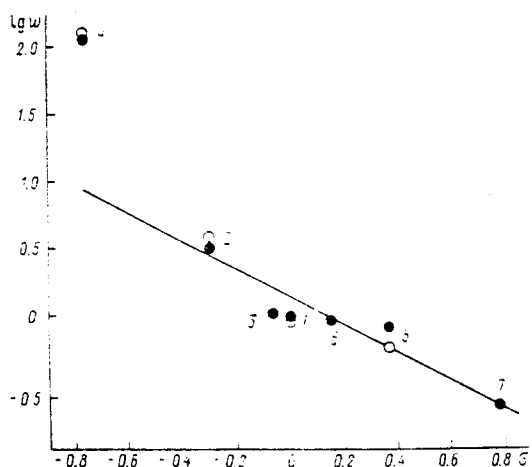


Fig. 1. Correlation of logarithmic relative rates w of oxidation of substituted toluenes in homogeneous conditions in CH_3COOH in thermal (open circles) and photochemical (filled circles) reactions with Brown σ^+ constants. The number of a circle corresponds to the number of the experiment shown in Table 1.

TABLE 1. Relative Rates of Oxidation of the Methyl Group in Substituted Toluenes $\text{XC}_6\text{H}_4\text{CH}_3$ by Cr(VI) Oxo Compounds

No.	Substituent X	Thermal reaction	Photochemical reaction	
			in CH_3COOH	in two-phase system
1	H	1.0	1.0	1.0
2	p- CH_3	4.0	3.2	3.3
3	m- CH_3		1.0	
4	p- OCH_3	120	120	12
5	m-Cl	0.55	0.8	1.5
6	p-Br		0.9	
7	p- NO_2		0.2	

It seems that the role of light in the oxidation of alkylarenes is to enhance the oxidative properties of the Cr(VI) species and to accelerate electron transfer to this species and proton (i.e., hydrogen-atom) transfer from the substrate. It is well known that light accelerates electron-transfer processes [7, 8]. The agreement of ρ^+ values for thermal and photochemical reactions may indicate that hydrogen-atom transfer is a key stage in both cases. There is evidence for formation of Cr(V) and Cr(IV) derivatives during thermal oxidation of alkylarenes [9]. Photochemical oxidation by Cr(VI) compounds has been studied in most detail in reactions with alcohols [10]. In this case, the process involves intermediate formation of a complex chromate-ion ester, transfer of p electrons from the oxygen atom to the 3d level of the chromium atom occurring during photolysis. Chromium(VI) oxo compounds are excited by light quanta with wavelength between 366 and 436 nm, the quantum yield in oxidation of alcohols being independent of wavelength in this range.

EXPERIMENTAL

Photochemical Reaction in CH_3COOH . A solution of $5 \cdot 10^{-4}$ g-mole CrO_3 and two substituted toluenes (each in tenfold molar excess) in 20 ml CH_3COOH was placed in a cylindrical vessel cooled to 7°C by a water jacket; the solution was then exposed, with vigorous stirring, to the total light from a DRSh-1000 (1000 W) high-pressure mercury lamp. Water (20 ml) was added to the solution, which was then extracted with chloroform (3×10 ml). The extract was washed with water, NaHCO_3 solution, and water and dried with Na_2SO_4 . The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (with benzene as eluant). The ratio of aldehydes formed was determined by integration of the CHO group

singlet signals in the PMR spectrum (using a Bruker SXP-4-100 spectrometer at 90 MHz). The components used in the competing reactions were as follows (reaction time and ratio of aldehydes, calculated per methyl group, are shown in parentheses): p-xylene-toluene (20 min, 3.2:1; 45 min, 4.0:1); m-xylene-toluene (60 min, 1.0:1.0); p-methoxytoluene-p-xylene (30 min, 37:1); m-chlorotoluene-toluene (30 min, 0.8:1.0); p-bromotoluene-m-chlorotoluene (180 min, 1.1:1.0); p-bromotoluene-p-nitrotoluene (270 min, 4.3:1).

Thermal Reaction. A solution of 0.05 g CrO₃ and two substituted toluenes (each in tenfold excess) in 5 ml CH₃COOH was kept at 70°C with stirring. The aldehydes formed were analyzed as described above. The following substrate pairs were used: p-xylene-toluene (15 min, 4.0:1); p-methoxytoluene-p-xylene (8 min, 30:1); m-chlorotoluene-toluene (45 min, 0.55:1.0).

Photochemical Reaction in a Two-Phase System. A mixture of a solution of 0.059 g K₂Cr₂O₇, 0.1 g Bu₄NBr, and 0.2 ml conc. H₂SO₄ in 20 ml H₂O with two aromatic compounds (1 ml toluene, 1.2 ml p-xylene, and 1.3 ml m-chlorotoluene were used) was exposed, with vigorous stirring, to a DRSh-1000 high-pressure mercury lamp. The ratio of oxidation rates was determined for the following substrate pairs: p-xylene-toluene (120 min, 3.3:1); m-chlorotoluene-toluene (120 min, 1.5:1.0); p-methoxytoluene-p-xylene (100 min, 3.8:1).

CONCLUSIONS

The logarithmic relative rates of oxidation of ring-substituted toluenes by Cr(VI) oxo compounds in CH₃COOH, stimulated by heat at 70°C or by exposure to light with $\lambda > 300$ nm at 7°C, correlate with the Brown σ^+ constants with ρ^+ equal to -1.05.

LITERATURE CITED

1. G. B. Shul'pin, E. Mácová, and P. Lederer, Zh. Obshch. Khim., 59, No. 11, 2604-2611 (1989).
2. G. B. Shul'pin, P. Lederer, and E. Mácová, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2638-2639 (1986).
3. Y. Ogata, A. Fukui, and S. Yugushi, J. Am. Chem. Soc., 74, No. 11, 2707-2709 (1952).
4. K. B. Wieberg and R. J. Evans, Tetrahedron, 8, No. 3/4, 313-335 (1960).
5. G. Cainelli and G. Cardillo, Chromium Oxidations in Organic Chemistry, Springer, Berlin (1984), p. 19-23, 37-41.
6. E. S. Rudakov, Reactions of Alkanes with Ozidizing Agents, Metal Complexes, and Radicals in Solution [in Russian], Naukova Dumka, Kiev (1986), pp. 121-122.
7. O. A. Reutov, I. P. Beletskaya, G. A. Artamkina, and A. N. Kashin, Reactions of Organometallic Compounds as Redox Processes [in Russian], Nauka, Moscow (1981).
8. G. B. Shul'pin, Organic Reactions Catalyzed by Metal Complexes [in Russian], Nauka, Moscow (1988).
9. V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York (1970).
10. F. Freeman, C. R. Armstead, and M. Y. Essig, J. Chem. Soc., Chem. Commun., No. 2, 65-66 (1980).