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Kinetics and Mechanism of Acid-Catalyzed Oxidation of Substituted Toluenes by Pyridinium Fluorochromate

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The kinetics of oxidation of substituted toluenes by pyridinium fluorochromate(VI) (PFC), $C_5H_5\overset{+}{N}HCrO_3F^-$, in aqueous acetic acid, in the presence of perchloric acid, have been studied. The main products are the corresponding aldehydes. While each of the oxidation is first order with respect to the oxidant, the rate is almost independent of the substrate concentration. The reactions depend on the first power of the concentration of acid. A kinetic isotope effect, $k_H/k_D=5.4$ at 30 °C, was observed. Electron-releasing groups were found to moderately facilitate the reaction, whereas the electron-withdrawing groups were found to have a retardation effect. Correlation with σ value yielded a ρ value of -2.0. The reaction does not induce polymerization of acrylonitrile. The effects of temperature and solvent compositions were studied and activation parameters evaluated. These and related data suggest that the initial reaction involves hydrogen abstraction forming an intermediate which subsequently produces the corresponding aldehyde.

Though the kinetics and mechanism of oxidation reactions using chromium(VI) oxidants are fairly well studied,[1–5] yet these reagents do not prove to be very satisfactory especially when some specific oxidations like oxidation of hydrocarbons, alcohols, thioethers etc. are desired. In recent years significant improvements were achieved by the use of pyridinium chlorochromate(VI) (PCC).[6–18] Of late, another effective chromium(VI) oxidant, pyridinium fluorochromate(VI) (PFC), $C_5H_5\overset{+}{N}HCrO_3F^-$, has been reported[19] which has several additional advantages over PCC, e.g., less acidity, selective oxidations under mild conditions, better solubility in nonaqueous solvents etc.

The oxidation of hydrocarbons is considerably less well understood and always present a mechanistic puzzle. In continuation with our interest in this subject,[20,21] we report in this investigation a detailed study of the kinetics and mechanism of the oxidation of side chains of mononuclear aromatic hydrocarbons such as toluene and substituted toluenes to their corresponding aldehydes. The common oxidizing agents (a) completely destroy the compound, (b) attack the nucleus, or (c) effect electrophilic substitution. The objective of the present investigation is not only to develop methods for oxidation of alkylarenes to the important aldehydes but also to get an insight to the reaction pathway.

Experimental

Materials. All the substrates were E. Merck grade and were purified by chromatography over alumina followed by distilation or recrystallization. Acetic acid (E. Merck) was distilled before use (bp 116 °C). Perchloric acid was a 'Baker analyzed' sample. $ArCD_3$ were prepared by the lithium aluminum deuteride reduction of their trichloromethyl derivative using the procedure reported earlier.[22] The materials used in the kinetic runs were repurified by chromatography and was shown to contain an insignificant amount of unlabeled, monodeuterio-, or dideuteriotoluenes, by the NMR spectra. Pyridinium fluorochromate (PFC) was synthesized by the method described in the literature.[19] The purity was checked by IR and UV analyses. The ionic strength of the medium was maintained constant by using sodium perchlorate, a Fluka purum product.

Kinetic Measurements. Both the substrate and oxidant solutions were thermostated and 30 °C for 3 h under nitrogen, and then mixed in equal volumes. The reaction mixture was homogeneous throughout the duration of the reaction. The reactions were followed by monitoring the absorption band at 444 nm, using a UV-VIS Beckmann spectrophotometer. This wavelength is the maximum absorption due to PFC, the absorption due to other reaction species being negligible. The reactions were performed under pseudo-first-order conditions by maintaining a large excess (10 times or greater) of the toluenes over PFC. Computations of the rate constants were made from the plot of log [PFC] against time. All infrared measurements were recorded on a Perkin-Elmer model 297 spectrophotometer and all NMR spectra were recorded on an EM-390 (Varian) 90-MHz spectrometer.

Product Analysis. The reactions were carried out in a manner similar to the kinetic experiments (using an excess of the substrate) and were allowed to proceed to completion in an atmosphere of nitrogen. The reaction mixture was diluted with ice-water saturated with sodium chloride, and was extracted several times with ether. The ether extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The material thus obtained was chromatographed over alumina, the toluene and xylenes being eluted with petroleum ether, and the corresponding aldehydes being eluted with 1:3 ether–petroleum ether. In each case, only toluene, xylenes, and the corresponding aldehydes were isolated. The aldehydes were characterized as the 2,4-dinitrophenylhydrazones, further characterized by using a standard method,[23] and confirmed by IR analyses.

Results and Discussion

Stoichiometry. Reaction mixtures containing an

Table 1. Rate Data for Oxidation of Toluene and Xylenes at 30±0.1 °C[a)]

[Substrate]	[PFC]	[$HClO_4$]	$10^4 \times k_1/s^{-1}$			
$M^{\dagger} \times 10^{-3}$	$M \times 10^{-4}$	M	*p*-Xylene	*o*-Xylene	*m*-Xylene	Toluene
1.0	1.0	0.15	5.03	3.16	2.38	1.45
5.0	1.0	0.15	5.70	3.83	2.91	1.87
10.0	1.0	0.15	6.06	4.11	3.27	2.29
50.0	1.0	0.15	6.78	4.74	3.85	2.80
100.0	1.0	0.15	7.43	5.23	4.36	3.33
10.0	2.0	0.15	6.14	4.24	3.17	2.51
10.0	3.0	0.15	6.31	4.38	3.48	2.34
10.0	4.0	0.15	6.40	4.19	3.26	2.27
10.0	5.0	0.15	6.15	4.23	3.14	2.16
10.0	1.0	0.10	4.10	2.70	2.15	1.53
10.0	1.0	0.20	8.18	5.60	4.25	3.10
10.0	1.0	0.25	10.20	7.10	5.31	3.85
10.0	1.0	0.30	12.02	8.25	6.60	4.55
10.0	1.0	0.15	5.38[b)]	3.43[b)]	2.60[b)]	1.63[b)]
10.0	1.0	0.15	6.75[c)]	4.80[c)]	4.01[c)]	2.98[c)]
10.0	1.0	0.15	7.45[d)]	5.50[d)]	4.65[d)]	3.67[d)]

a) [$NaClO_4$]=0.155 M; HOAc: H_2O=95: 5 (v/v). b) 25 °C; c) 35 °C; d) 40 °C; (error limit: ±0.1 °C).
† 1 M = 1 mol dm^{-3}.

excess of the oxidant (PFC) were allowed to react to completion under a nitrogen atomosphere at 30 °C and then analyzed spectrophotometrically for unchanged PFC and also by iodometric determination of the unreacted chromium(VI). The results gave a ratio of substrate and oxidant as 1:2, according to the equation:

$$XC_6H_4CH_3 + 2Cr^{6+} + H_2O \longrightarrow XC_6H_4CHO + 2Cr^{4+} + 4H^+ \ (X = CH_3, OCH_3, Cl, Br). \qquad (1)$$

This equation corroborates to a two-electron transfer and is in agreement with the proposal of Brown et al.,[24)] who recently reported that the exact nature of the reaction product of PFC is not known. The idea is also supported from a recent report.[25)] About 75—80% of the hydrocarbons were oxidized and about 80—85%, based on the hydrocarbons consumed, of the corresponding aldehydes were obtained.

Kinetic Results. The reactions were found to be first order with respect to the oxidant and near zero order in substrate (Table 1). The observed small but steady increase in the rate constant values for the hydrocarbons with increasing concentrations of the substrate and a plot of log k_1 against substrate concentrations show that the rates increase in very small fractions with the sequential increase in substrate concentration. This implies a probable complex formation between the substrate and the oxidant.

The order with respect to perchloric acid was determined in the same way (Table 1). A plot of log k_1 against log [H^+] gave a linear relationship with a slope of nearly unity. An attempt was made to correlate the rate data with the Hammett acidity function (H_0). Using H_0 values from Wiberg's data,[5)] plots of log k_1 against H_0 gave slopes far different from unity. Thus under the present experimental conditions, it seemed appropriate to correlate the rates of these reactions with [H^+] rather than with H_0.

Table 2. Effect of Solvent Compositions at 30.0±0.1 °C[a)]

HOAc : H_2O	$10^4 \times k_1/s^{-1}$		
%; v/v	*p*-Xylene	*o*-Xylene	*m*-Xylene
80 : 20	1.01	0.98	0.82
85 : 15	1.62	1.22	1.06
90 : 10	3.18	2.30	2.01
95 : 5	6.06	4.11	3.27

a) [Xylenes]=10×10^{-3} M; [$HClO_4$]=0.15 M; [PFC]=1×10^{-4} M; [$NaClO_4$]=0.155 M.

Table 3. Kinetic Isotope Effect at 30.0±0.1 °C[a)]

Substrate	$10^5 \times k_1/s^{-1}$		
	$ArCH_3$ (k_H)	$ArCD_3$ (k_D)	k_H/k_D
p-$CH_3C_6H_4$-	60.6	11.0	5.4
o-$CH_3C_6H_4$-	41.1	8.0	5.1
m-$CH_3C_6H_4$-	32.7	6.0	5.4

a) [Substrates]=10×10^{-3} M; [PFC]=1×10^{-4} M; [$HClO_4$]=0.15 M; [$NaClO_4$]=0.155 M; HOAc : H_2O=95 : 5 (v/v).

The rates of the reactions were found to be unaffected by changes in the ionic strength of the medium. Similar observations were also reported earlier.[26—28)] The oxidation processes were also studied in solutions containing varying proportions of acetic acid and water (Table 2). The reaction rate decreases with increase in dielectric constant of the medium suggesting that more polar solvents may require longer reaction time for the oxidation.[15)] A plot of log k_1 against the inverse of dielectric constants of the media is a straight line with positive slope and implies the occurrence of an interaction between a dipole and a positive ion.[29)]

A kinetic isotope effect, k_H/k_D=5.4, was observed (Table 3), indicating that the rate-determining step

Table 4. Effect of Substituents at 30.0±0.1 °C

[Substrate]	Substituted toluene	k/k_H
0.01 M	$10^4 \times k_1/s^{-1}$	
p-Methoxy	19.70	8.60
p-Methyl	6.06	2.64
m-Methyl	3.27	1.43
H	2.29	1.00
p-Chloro	0.81	0.35
p-Bromo	0.74	0.32
m-Chloro	0.38	0.16

[PFC]=1×10^{-4} M; [$HClO_4$]=0.15 M; [$NaClO_4$]=0.155 M; HOAc : H_2O=95 : 5 (v/v).

Table 5. Activation Parameters for the Oxidation Reactions

Substrate	ΔH^*	$-\Delta S^*$	ΔG^*
	$kJ\,mol^{-1}$	$J\,mol^{-1}\,K^{-1}$	$kJ\,mol^{-1}$
Toluene	39.6	184.0	95.3
p-xylene	14.9	257.5	92.9
o-xylene	19.9	244.3	93.9
m-xylene	14.9	245.0	94.2

Error limit for ΔH^*, ΔS^*, and ΔG^* (at 303 K) are $\pm 2.5\,kJ\,mol^{-1}$, $\pm 4.0\,J\,mol^{-1}\,K^{-1}$, and $\pm 3.0\,kJ\,mol^{-1}$ respectively.

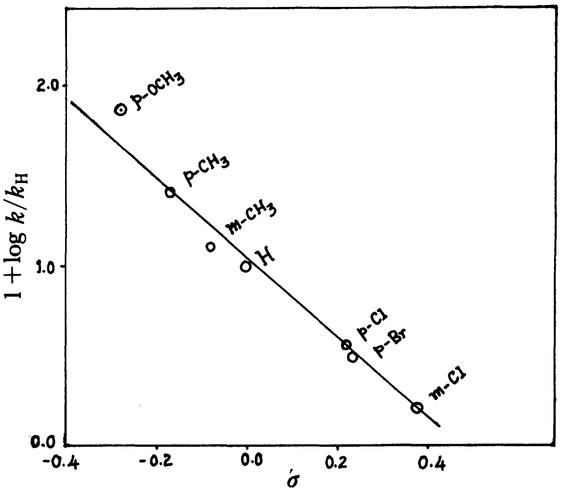


Fig. 1. Plot of log k/k_H against σ values for the oxidation of substituted toluenes at 30°C (Hammett Plot).

involved the cleavage of the carbon-hydrogen bond of the methyl group attached to the arene ring.

The oxidation was studied at different temperatures (vide Table 1) and the activation parameters have been evaluated (Table 5).

The effect of substituents was also determined (Table 4). A plot of the logarithm of the relative rates of reaction against the Hammett σ values gave a fair fit to a straight line with a slope of approximately −2.0 (Fig. 1).

The oxidation reaction, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, no signal of radicals could be detected in the ESR spectra of each of the reactions carried out in a flow system (recorded on an E-4, Varian, EPR spectrometer). In control experiment without hydrocarbon, the concentration of PFC did not change.

The observed acid dependence of the reaction suggests that the reaction may be one between the alkylarenes and a protonated species of chromium(VI). This view is further supported[27)] by the observance of linear plot of log k_1 against inverse of dielectric constant, and is in accord with the involvement of such species well established in chromium trioxide oxidation.[5,30)] Again the observed ρ value (−2.0) does neither conclusively opt for a radical nor an ionic pathway. However, it implies that transfer of hydrogen nucleus is the essence of the mechanism of such reactions. The near constancy of the free energy of activation shows that the same mechanism is operative in all these oxidation processes.

Moreover, the order with respect to the substrate (Table 1) is almost but not quite zero, suggesting a multistep reaction sequence via the formation of an intermediate complex between the substrate and PFC.

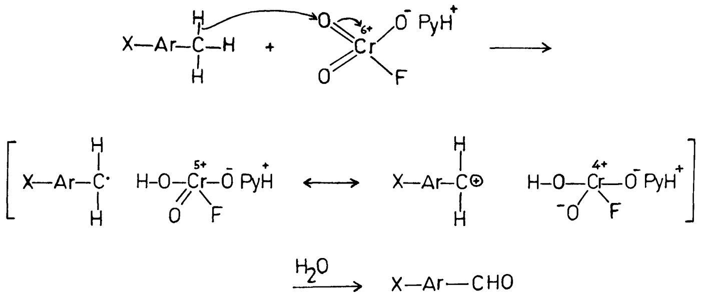
Though the reaction failed to give any significant ESR signal and to induce polymerization of acrylonitrile, the hydrogen abstraction mechanism cannot be ruled out as the initially-formed radical would be expected to react instantaneously with the Cr^{5+} species formed in the initial step. This observation is known to occur in the oxidation of saturated hydrocarbons by Cr(VI) compounds.[5,30)] Again the large negative reaction constants (also ρ value) together with the substantial deuterium isotope effect indicate a considerable carbonium ion character in the transition state.

Thus the oxidation of the aromatic nuclei would appear to involve hydrogen transfer through an intermediate complex based on the following two mechanism:

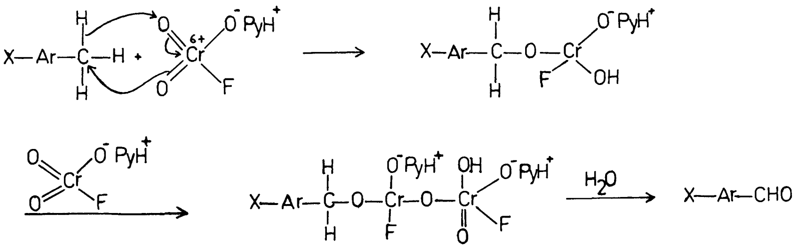
(i) The intermediate complex consisting of a radical and a Cr^{5+} species or a carbonium ion and a Cr^{4+} species (Sceheme 1). The ambiguity regarding the intermediate could be overcome by considering the complex as a resonance hybrid in which the carbon atom has both radical and carbonium ion characters. This type of intermediate has also been reported earlier.[21,31–34)]

(ii) Alternatively, it could be via the formation of an Etard type[35)] complex as the intermediate (Scheme 2). Though no precipitate of the complex was observed yet it may be argued that owing to immediate hydrolysis no isolation of the intermediate was possible. Similar observation has been reported earlier in the chromium trioxide oxidation in aqueous acetic acid solution.[36)]

However, as the intermediate complex could not be isolated, neither magnetic susceptibility study nor ESR study of the complex could be performed.



Scheme 1.



Scheme 2.

Moreover, the formation of Etard complex is not very much favorable in acetic acid medium.[35] Thus it seems reasonable to believe that the oxidation mechanism shown in Scheme 1 is the likely one involved in the present cases. Since the hybrid would have a lower energy than either of the two pairs, the stability of the intermediate could be expected. A large negative entropy of activation obtained in the present study may also support the view.

So the overall oxidation of the substituted toluenes would appear to involve initial electron transfer from the substituent group of the side chain hydrocarbon to the oxidant and the subsequent reaction of the resulting intermediate with the nucleophiles in the reaction solution to the formation of the products.

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References

1) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

2) G. T. E. Graham and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030 (1958).

3) J. O. Edwards, *Chem. Rev.*, **50**, 455 (1952).

4) K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3032 (1958).

5) K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York (1965), pp. 71, 98—105.

6) E. J. Corey and G. W. J. Fleet, *Tetrahedron Lett.*, **1973**, 4499.

7) J. R. Holum, *J. Org. Chem.*, **26**, 4814 (1961).

8) A. Bowers, T. G. Hatshall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, **1953**, 2555.

9) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, **1968**, 3363.

10) H. H. Sisler, W. C. L. Ming, E. Metter, and F. R. Hurley, *J. Am. Chem. Soc.*, **75**, 446 (1953).

11) F. S. Guziec, Jr. and F. A. Luzzio, *Synthesis*, **1980**, 691.

12) J. C. Collins and W. W. Hess, *Org. Synth.*, **52**, 5 (1972).

13) E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, **1979**, 399.

14) G. I. Poos, G. E. Aoth, R. E. Beyber, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 425 (1953).

15) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **1975**, 2647.

16) E. J. Corey and D. L. Boger, *Tetrahedron Lett.*, **1978**, 2461.

17) W. G. Dauben and D. M. Michno, *J. Org. Chem.*, **42**, 682 (1972).

18) G. Piancatelli, A. Scettri, and M. D'Auria, *Tetrahedron Lett.*, **1977**, 2199.

19) M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Synthesis*, **1982**, 588.

20) A. K. Bhattacharjee and M. K. Mahanti, *Int. J. Chem. Kinet.*, **14**, 1113 (1982); *Indian. J. Chem.*, **22B**, 74 (1983); *React. Kinet. and Cat. Lett.*, **22**, 227 (1983); *Bull. Korean Chem. Soc.*, **4**, 102 (1983); *Gazz. Chim. Ital.*, **1983**, 113; *Bull. Soc. Chim. Fr.*, **1983**, I-270.

21) B. Bhattacharjee, M. N. Bhattacharjee, M. Bhattacharjee, and A. K. Bhattacharjee, *Int. J. Chem. Kinet.*, **17**, 629 (1985).

22) R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

23) A. I. Vogel, "A Text Book of Practical Organic Chemistry," ELBS & Longman, London (1958), p. 758.

24) H. C. Brown, C. Gundu Rao, and S. U. Kulkarni, *J. Org. Chem.*, **44**, 2809 (1979).

25) K. Rajasekharan, T. Baskran, and C. Gnanasekaran, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 1183.

26) G. V. Bakore, K. K. Banerjee, and R. Shankar, *Z. Phys. Chem. (Frankfurt)*, **45**, 129 (1965).

27) K. K. Banerjee, *J. Chem. Soc., Perkin Trans. 2*, **1978**,

639; *Bull. Chem. Soc. Jpn.*, **51**, 2732 (1978).

28) M. N. Bhattacharjee, M. K. Chaudhuri, and H. S. Dasgupta, *Bull. Chem. Soc. Jpn.*, **57**, 258 (1984).

29) E. S. Amiss, "Solvent Effects on Reaction Rates and Mechanism," Academic Press, New York (1967), p. 42.

30) K. B. Wiberg and G. Fester, *J. Am. Chem. Soc.*, **83**, 423 (1961).

31) J. Roček, *Tetrahedron Lett.*, **1962**, 135.

32) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).

33) O. C. Musgrave, *Chem. Rev.*, **69**, 499 (1969).

34) R. N. Adams, *Acc. Chem. Res.*, **2**, 175 (1967).

35) W. H. Hartford and M. Darrin, *Chem. Rev.*, **58**, 1 (1958).

36) R. Slack and W. A. Waters, *J. Chem. Soc.*, **1949**, 599.