

SURFACE PHOTOCHEMISTRY: THE PHOTO-CHLORINATION OF AROMATIC
HYDROCARBONS WITH FERRIC CHLORIDE ON ALUMINA

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SUMMARY: Irradiation of a number of aromatic hydrocarbons adsorbed on alumina in the presence of ferric chloride leads to monochlorination.

A number of thermally-induced halogenations of aromatic hydrocarbons in the presence of cupric¹ or ferric² halides have been reported. These reactions were carried out by heating the reagents in a high-boiling solvent (e.g. nitrobenzene, chlorobenzene) and were rather complex, usually a mixture of chloro compounds being obtained. Even under these drastic conditions, chlorination of naphthalene or phenanthrene was not successful.¹ The cation radical, the expected reactive intermediate in these reactions, has been generated in conc. sulfuric acid or with other oxidizing agents,³ and its reaction with nucleophilic reagents reported.⁴ In addition, the observation of the cation radical of polycyclic aromatic hydrocarbons adsorbed on alumina (perylene in particular) by ESR is well established.⁵ It seemed to us that electron transfer from the hydrocarbon should be facilitated in the excited state, and preliminary observations appeared to confirm this.⁶ It is known that activated alumina has two different types of active sites, one has electron-donor^{7,8} properties and the other has electron-acceptor⁵ properties. Oxygen is required to enhance the electron-acceptor properties of alumina which generate the cation radicals of the hydrocarbon.⁵ Irradiation of phenanthrene on acidic alumina, which contains traces of HCl, produced 9-chlorophenanthrene in minuscule amounts (<1%), but encouraged us to look further. We report here the results of the irradiation of aromatic hydrocarbons adsorbed on alumina in the presence of excess ferric chloride.

The hydrocarbon (ca. 25 mg/g) (Table) was irradiated at ca. 350 nm (Rayonet) on the surface of activated alumina coated with ferric chloride (0.1 g/g) in a rotating open tube for 20 hrs. The product was isolated by extraction and identified by comparison with an authentic specimen. Those hydrocarbons (naphthalene, phenanthrene) with higher oxidation potentials (Table) required ferric chloride, alumina and light for reaction affording 1-chloronaphthalene and 9-chlorophenanthrene respectively. Substitution of silica gel for

TABLE

VARIATION IN CHLORINATION CONDITIONS

Compound	Ox. Potential(V) ^a	Conditions	Product	% Yield ^b (% recovery)
Naphthalene	1.54	hv,c Al ₂ O ₃	1-Cl	27 (13)
		hv,c SiO ₂	—	No reaction
Phenanthrene	1.50	hv,c Al ₂ O ₃	9-Cl	26 (19)
		hv,d Al ₂ O ₃	9-Cl	18 (56)
		hv,c SiO ₂	—	No reaction
Pyrene	1.16	hv,c,e Al ₂ O ₃	1-Cl	6.5 (18)
		c,f Al ₂ O ₃	1-Cl	3.4 (21)
Anthracene	1.09	c,f Al ₂ O ₃	9-Cl	40 (7.8)
		d,f Al ₂ O ₃	9-Cl	29 (31)
		c,f SiO ₂	9-Cl	17 (10)

^a Against SCE. cf. C.K. Mann and K.K. Barnes, "Electrochemical Reactions in Non-aqueous Systems", M. Dekker Inc. N.Y. (1970).

^b absolute yield.

^c air.

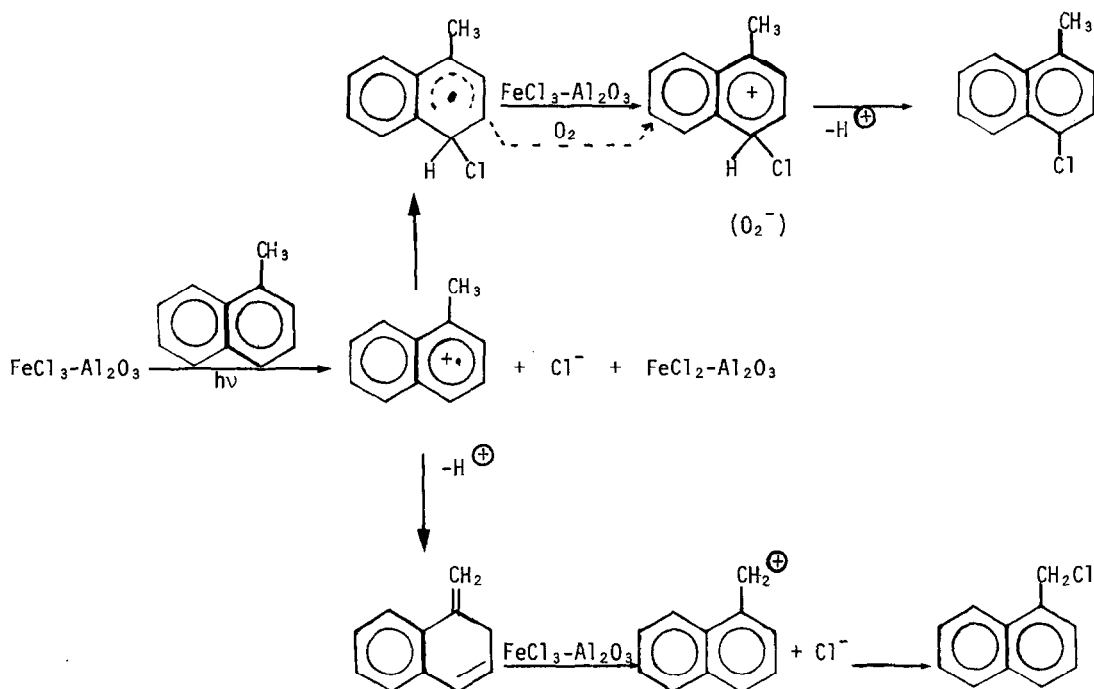
^d degassed.

^e irradiation accelerated the reaction.

^f dark reaction at room temperature.

alumina, or omission of light led to no reaction; so, also did the irradiation on solid ferric chloride. Pyrene and anthracene, with lower oxidation potentials (Table) were, however, chlorinated with ferric chloride at room temperature on alumina in the absence of light to give 1-chloropyrene and 9-chloroanthracene respectively though the chlorination of pyrene was accelerated by irradiation. The chlorination of anthracene also proceeded on silica gel coated with ferric chloride without light. The omission of the alumina surface led to the formation of more complex mixtures. Degassing of sample (anthracene, phenanthrene) slowed the reaction whilst water, required for the ferric chloride chlorination of toluene,⁹ in small amount (15 mg) inhibited the photochlorination of phenanthrene on alumina. Addition of water also inhibits strongly electron-acceptor or electron-donor properties of alumina.^{8,10} Photochlorination of 1-methylnaphthalene with ferric chloride on alumina afforded a mixture of nuclear-chlorinated naphthalene and chloromethylnaphthalene, the former predominating by 2:1 from NMR measurement of the reaction mixture. Although sidechain chlorination is often an indication of a radical process we believe that in the present instance the observation is consistent with a cation-radical intermediate (Scheme).

SCHEME



The recovery of the aromatic hydrocarbons was poor: this is attributed to oxidative polymerization of the cation radical.^{5,11} Much of the material could not be eluted from the alumina surface.

The formation of the cation radicals of aromatic compounds on alumina is reinforced by a co-adsorption of a strong electron-acceptor such as trinitrobenzene.¹² We presume the ferric chloride, a strong Lewis acid, increases the electron-acceptor properties of alumina, as indicated in the tentative scheme, producing chloride ion. The cation radical then adds the chloride ion, the resultant radical being further oxidized by excess ferric chloride (or oxygen) to the chlorinated hydrocarbon. In this sequence, it is the ferric chloride which is presumed activated, and further study revealed that this was the case. Reduction of the quantity of ferric chloride, still greatly in excess of stoichiometric, so that more light could be adsorbed by the phenanthrene led to a reduction in the rate of chlorination. The study is being continued.

References:

1. J.C. Ware and E.E. Borchert, *J. Org. Chem.*, **26**, 2263, 2267 (1961); D.C. Nonhebel, *J. Chem. Soc.*, 1216 (1963).
2. P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 759, 762 (1961); J. van Dijk, J.J. van Daalen and G.B. Paerels, *Rec. Trav. Chim.*, **93**, 72 (1974); A. Kohda, K. Ueda and T. Sato, *J. Org. Chem.*, **46**, 509 (1981).
3. W. Ij Aalbersberg, G.J. Hoijtink, E.L. Mackor and W.P. Weijland, *J. Chem. Soc.*, 3049 (1959); J.J. Rooney and R.C. Pink, *Proc. Chem. Soc.*, 70, 142 (1961).
4. H.J. Shine and C.V. Ristango, *J. Org. Chem.*, **37**, 3424 (1972); J.K. Kochi, R.T. Tang and T. Bernath, *J. Am. Chem. Soc.*, **95**, 7114 (1973); A. Ledwith and P.J. Russell, *J.C.S. Chem. Commun.*, 291, 959 (1974); M.K. Logani, W.A. Austin and R.E. Davies, *Photochem. Photobiol.*, **33**, 143 (1981).
5. D.B. Flockhart, J.A.N. Scott and R.C. Pink, *Trans. Farad. Soc.*, **62**, 730 (1966); B.D. Flockhart, I.M. Sesay and R.C. Pink, *J.C.S. Chem. Commun.*, 439 (1980).
6. Dr. S.K. Wong, unpublished data, personal communication. We thank Dr. Wong for this information.
7. B.D. Flockhart, S.S. Uppal and R.C. Pink, *Trans. Farad. Soc.*, **67**, 513 (1971); D.B. Flockhart, L. McLoughlin and R.C. Pink, *J. Catalysis*, **25**, 305 (1972).
8. D.B. Flockhart, I.R. Leith and R.C. Pink, *Trans. Farad. Soc.*, **65**, 542 (1969).
9. H. Inoue, M. Izumi and E. Imoto, *Bull. Chem. Soc. Japan*, **47**, 1712 (1974).
10. J.J. Rooney and R.C. Pink, *Trans. Farad. Soc.*, **58**, 1632 (1962).
11. P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960); P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).
12. B.D. Flockhart, I.R. Leith and R.C. Pink, *J. Catalysis*, **9**, 45 (1967).

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