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REACTIONS OF CHLORINE DIOXIDE IN DICHLOROMETHANE
I. FORMATION OF RADICAL CATIONS IN ACID MEDIA

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Abstract: Chlorine dioxide oxidises electron rich organic compounds to the corresponding radical cations in dichloromethane/TFA medium. In a different experimental set up using alkaline biphasic solvent system, its utility as hydrogen abstractor has been capitalized in the preparation of diazodiphenyl methane in good yield.

Many reports exist of chlorine dioxide oxidations in aqueous solutions[1] but very few studies have been made of such reactions in non aqueous media[2] and seemingly none in dichloromethane in which ClO_2 is appreciably stable and believably has a wider role to play. The most thoroughly studied reactions of ClO_2 with organic compounds are those involving oxidations of amines in aqueous solutions[3]. An ECE type mechanism has been shown to prevail in some of these reactions that involve radical cation intermediates while in other amines a hydrogen abstraction mechanism is suggested.

We now wish to report our findings about the reaction of ClO_2 in non aqueous solvents more specifically in dichloromethane.

Electron rich organic compounds of moderate oxidation potentials reacted with ClO_2 in CH_2Cl_2 in the presence of small amounts of TFA yielding deep coloured solutions whose electronic absorption spectra indicated radical cations having been formed. A general experimental procedure comprised adding a CH_2Cl_2 solution of ClO_2 ($\sim 0.5 \times 10^{-4}$M) to the organic compound ($\sim 0.5 \times 10^{-4}$M) in CH_2Cl_2 /TFA (9:1,v/v) solvent system at 15°. Besides recording the UV/Vis spectra of the generated species(Fig.1,3-6;Table 1), esr studies(Fig.2) of such solutions provided additional evidence of the corresponding radical cations having formed. All the reactions were carried out in air except that for obtaining esr spectra, deoxygenated solutions were used.

In some cases, particularly with those molecules having low ionization potentials an added TFA was not needed in the oxidation by ClO_2. This exemplifies a straight forward electron transfer having occured from the organic molecule to ClO_2(Eq.1).

$$ArH + ClO_2 \rightleftharpoons ArH^{\bullet+} + ClO_2^- \qquad (1)$$

Thus tetramethyl-p-phenylene diamine (TMPD), phenothiazine and tetrathiofulvalene were oxidised to their radical cations which, however, decomposed sooner as compared to their acidified solutions. This is presumably due to ClO_2^- not behaving as a stabilizing counter ion. The presence of TFA, however , makes a dramatic change in that the stability of radical cations in solution is drastically enhanced and even such compounds having appreciable oxidation potential like thianthrene and tetraphenyl ethylene are easily oxidised to radical cations.

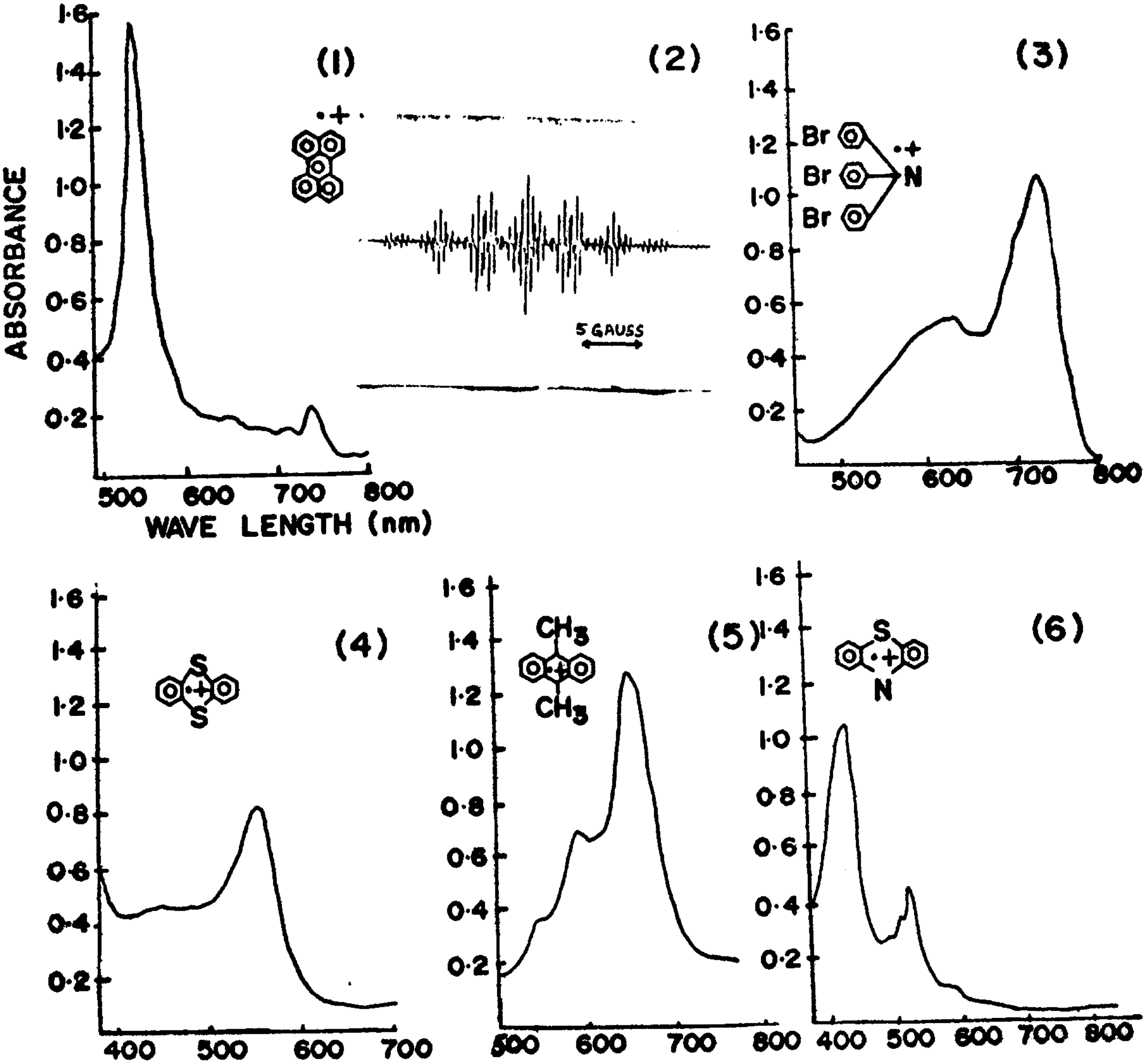

Fig.1 & Figs.3-6. Electronic absorption spectrum of Perylene, tris(p-bromophenyl) amine, thianthrene, 9,10-dimethyl anthracene and phenothiazine radical cations obtained by oxidation with chlorine dioxide in dichloromethane/TFA media(9:1 v/v). Fig.2. ESR spectrum of so formed perylene radical cation.

The primary role of acid is thought to be protonation of electron rich molecules and it is the protonated form that loses hydrogen atom to ClO_2 during radical cation formation (Eq.2).

$$\mathrm{ArH} + \mathrm{CF_3COOH} \rightleftharpoons \mathrm{ArH_2^+} + \mathrm{\bar{O}COCF_3}$$
$$\mathrm{ArH_2^+} + \mathrm{ClO_2} \rightleftharpoons \mathrm{ArH^{\bullet+}} + \mathrm{HClO_2}$$

$$\mathrm{ArH} + \mathrm{CF_3COOH} + \mathrm{ClO_2} \rightleftharpoons \mathrm{ArH^{\bullet+}} + \mathrm{\bar{O}COCF_3} + \mathrm{HClO_2} \quad ...(2)$$

The steps outlined in Eq.2 are reminiscent of mechanism suggested by Buck & co-workers[4] for the oxidation of aromatic molecules by quinones in strong acid (Eq.3).

$$2\mathrm{ArH_2^+} + \mathrm{Q} \rightleftharpoons 2\,\mathrm{ArH^{\bullet+}} + \mathrm{QH_2} \quad ...(3)$$

Oxidations by ClO_2 appear to be attractive alternatives to the already existing methods[5] of radical cation formation and after more work is done particularly in making a judicious selection of solvent-acid mixtures, ClO_2 oxidations might receive a wide-spread interest in preparation of isolable radical cation salts and in reactions where radical cations intervene.

Table 1: λ_{max} of cation radicals obtained in ClO_2 oxidations in CH_2Cl_2/TFA(9:1,v/v)

Substrate$^{\bullet+}$	Observed λ_{max} (nm)	Reported λ_{max} (nm)
1. TMPD[a]	614, 567.5	618, 567 [c]
2. Tetrathiofulvalene[a]	580.6, 438.5	580, 435 [d]
3. Phenothiazine[a]	512.2, 438.9	515, 437[e]
4. Ferrocene	619.5	619[f]
5. Tris(p-bromophenyl)amine	726.5	725[g]
6. Thianthrene	548.5	546[h]
7. 9,10-dimethylanthracene	667.5	b
8. Tetraphenyl ethylene	485.5	b
9. Perylene	542	540[i]
10. Pyrene	505	505[j]

a: TFA was not required, b: not located in literature, c: ref 6, d: ref 7, e: ref 8, f: ref 9, g: ref 10, h: ref 11, i: ref 12, j: ref 13.

Lastly, we wish to describe a simple method of preparing aliphatic diazo compounds, in particular diazodiphenyl methane (Ph_2CN_2) and its substituted analogs. The new method arose from our study on oxidation of e.g., benzophenone hydrazone with ClO_2 in CH_2Cl_2 solution. A purple colour appeared immediately upon mixing the reactants which remained for the first few minutes of the reaction.

Assuming that Ph_2CN_2 is formed as an intermediate as evidenced by the appearance of a purple colour, it was envisioned that the reaction could be terminated at the diazoalkane stage by using an alkaline biphasic solvent system. Thus by using a CH_2Cl_2-aqueous ammonia two phase system containing a phase transfer catalyst, tetra-n-butyl-ammonium hydroxide, a reasonably efficient and rapid method of preparing Ph_2CN_2 in 75% yield was evolved.

In its generality the reaction involves dehydrogenation of the hydrazone by ClO_2(Eq.4) and the efficacy of the method lies in the fact that any chlorous acid generated during the reaction is consumed by aq. NH_3 thereby preventing any follow-up reation of Ph_2CN_2.

$$Ph_2C{=}N.NH_2 \ + \ 2\ ClO_2 \ \longrightarrow \ Ph_2C{=}N_2 + 2\ HClO_2 \qquad ...(4)$$

In the absence of an alkaline medium, the unneutralised chlorous acid brings about acid induced decomposition of Ph_2CN_2 by a known mechanism[14].

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