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FORMATION OF FLUORO-MEISENHEIMER COMPLEXES USING HOMOGENEOUS AND HETEROGENEOUS FLUORIDE ION SOURCES

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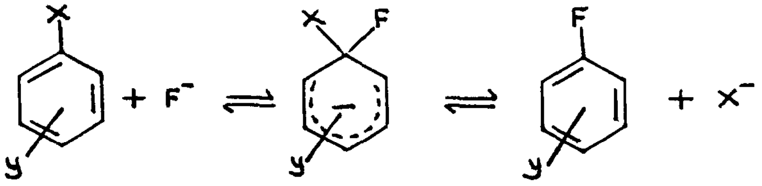
SUMMARY

1-Chloro-2,4-dinitrobenzene, 1-fluoro-2,4-dinitrobenzene and 1,3-dinitrobenzene form Meisenheimer complexes with tetra-n-butylammonium fluoride and alumina supported alkali metal fluorides. Both kinetically controlled and thermodynamically controlled complexes are observed.

INTRODUCTION

Nucleophilic aromatic substitution by fluoride is thought to occur via the formation of a Meisenheimer complex (i) although previous attempts to identify such complexes using reactive fluoride reagents such as KF-18-crown-6 have only succeeded with the highly activated 1,3,5-trinitrobenzene and 1-fluoro-2,4,6-trinitrobenzene [1,2]. As part of our



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programme of research on the development of fluoride ion sources we have investigated the interaction of the powerful homogeneous reagent tetra-n-butylammonium fluoride (TBAF) [3,4], and supported alkali metal fluorides, [5], with 1,3-dinitroaromatics. We now report our evidence for the formation of fluoro-Meisenheimer complexes containing only two stabilising nitro groups.

RESULTS AND DISCUSSION

Reaction of 1-chloro-2,4-dinitrobenzene with the so-called 'naked' fluoride reagent, KF-18-crown-6 in acetonitrile, has been reported as giving 1-fluoro-2,4-dinitrobenzene with no evidence of an intermediate Meisenheimer complex [2]. We have followed the progress of this reaction by ^{1}H n.m.r. spectroscopy and have observed the presence of a very weak doublet centred at ca. 6.2 p.p.m. which could be due to the presence of a σ-complex. Addition of KF-alumina or CsF-alumina to a solution of 1-chloro-2,4-dinitrobenzene in dimethylsulphoxide immediately produced an intense purple colour. The spectrum of the supernatant liquid from this mixture is shown in Figure 1, and is consistent with the presence of a σ-complex. On heating this solution to 50°C, the bands at ca .520 nm and ca.590 nm disappeared while those at 372 and 428 nm became more intense (Fig. 1). The more potent F^- source TBAF [4] reacted immediately with 1-chloro-2,4-dinitrobenzene in dimethylsulphoxide, acetonitrile or tetrahydrofuran at room temperature to give an intense purple solution. The spectrum of this solution showed weak bands at 590 and 520 nm, strong bands at 428 and 372 nm and no unreacted 1-chloro-2,4-dinitrobenzene (using a threefold excess of TBAF). Work-up of the reaction mixture gave the expected 1-fluoro-2,4-dinitrobenzene product (use of TBAF $3H_2O$ resulted in the formation of 2,4-dinitrophenol)

The ^{1}H n.m.r. spectrum of the reaction solutions showed the presence of proton resonances at higher field than those of the substrate (Table) consistent with a σ-complex.

^{1}H-^{1}H Spin-spin couplings in the complex are approximately the same as in the starting material making assignments straightforward (Table). No ^{1}H-^{19}F spin-spin coupling is

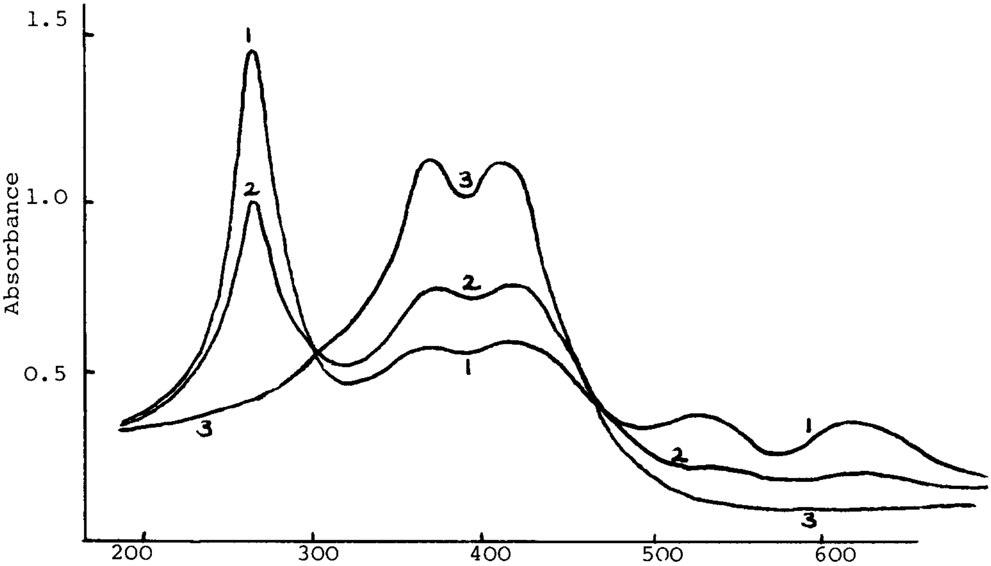


Fig. 1. Spectra of a solution of 1-chloro-2,4-dinitrobenzene in DMSO (0.00001M) over KF-alumina (0.00004M equiv. F^-) at 50°C after 0 hours (1), 1 hour (2), and 2 hours (3) (10 mm path length). A similar spectrum can be obtained using Bu_4NF (ca. 0.00003M equiv. F^-) although complete reaction of the starting material is achieved at room temperature.

observed presumably due to fast exchange in solution with excess F^- although at lower temperatures, the signals broaden. The ^{19}F chemical shift is consistent with that observed for trinitrobenzene complexes [2]. The relatively large change in chemical shift (1.85 p.p.m.) observed for the C-6 hydrogen (doublet, J = 9Hz) compared to those observed for the other hydrogens is consistent with structure I rather than the most probable alternative, structure II [6] (Figure 2).
This may be rationalised in terms of the valence bond structures for I which unlike those for II place the C-6 hydrogen in a less conjugated environment than the other hydrogens.

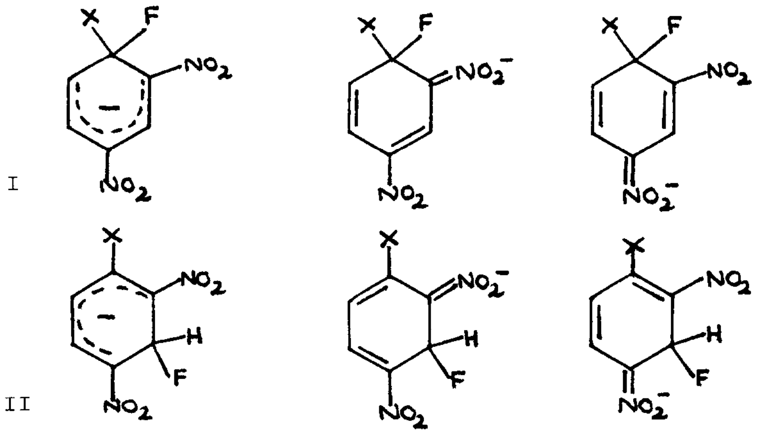


Fig. 2. The two most probable structures for the fluoro-Meisenheimer complex formed with 1-chloro-2,4-dinitrobenzene and their major valence bond structures.

Reaction of 1-fluoro-2,4-dinitrobenzene with KF-alumina in dimethysulphoxide produced an intense purple colour. The electronic absorption spectrum was almost identical to the higher energy part of that shown in Figure 1 (λ_{max} = 374 and 430 nm) although at no time were lower energy bands observed in the spectrum. The ^{1}H and ^{19}F n.m.r. spectra of the solution were also very similar to those observed for 1-chloro-2,4-dinitrobenzene with KF-alumina (Table). The ^{1}H-^{19}F spin-spin coupling observed in the parent is lost in the complex due to fast exchange. These observations suggest that we may be observing the same species in both systems (structure I in Figure 2, X = F). The downfield shift in the ^{19}F chemical shift of the complex relative to the starting material is consistent with previous observations [2].

It has been found that the formation of complexes by addition of anions at ring-carbons carrying hydrogen is a much faster process than addition at ring-carbons carrying other groups presumably for steric reasons [7]. It is possible therefore, that the lower energy bands initially observed in the electronic absorption spectrum of the F^--1-chloro-2,4-

dinitrobenzene system are due to structure II (Fig. 2). In order to test this hypothesis we have studied the reaction of 1,3-dinitrobenzene with F^-. The lack of an electropositive carbon carrying halogen in this molecule should reduce the rate of decomposition of II (X = H) to I (X = H). Addition of CsF - alumina or TBAF to a solution of 1,3-dinitrobenzene in dimethylsulphoxide resulted in the immediate formation of a blue colour. The electronic absorption spectrum of the solution (Fig. 3) shows bands at 680, 570, 440 and 365 nm. All of these bands remained intense over a period of several hours consistent with the presence of two stable σ-complexes such as I (X = H) and II (X = H). Fresh solutions of 1,3-dinitrobenzene containing a large excess TBAF in acetonitrile or dimethylsulphoxide show short-lived visible bands at 530 and 730 nm (as well as the other bands described earlier). In dilute solutions these bands disappear within minutes and may well be due to short-lived charge transfer intermediates involving more than one F^- (a similar effect has been observed for solutions of aromatic nitro-compounds containing cyanide ions [8].

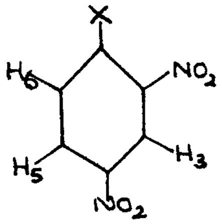
The ^1H n.m.r. of a fresh solution of 1,3-dinitrobenzene and excess TBAF in CD_3CN is quite different to those observed for the halo-dinitrobenzene-F^- mixtures. Several new peaks are observed in the 8.6 - 4.0 p.p.m. region of the spectrum. The spectrum is extremely complex and difficult to interpret although the presence of two broad peaks in the 5.5 - 4.0 p.p.m. region of the spectrum is consistent with two sp^3 F-carrying carbons (C-1, X=H in structure I and C-3, X=H in structure II).

Similar results to those described above can be obtained using polar solvents other than dimethylsulphoxide or acetonitrile such as dimethylformamide and acetone. Addition of a supported fluoride to a benzene or toluene solution of 1-chloro-2,4-dinitrobenzene for example, immediately resulted in an intense purple colour on the support but not in the solvent. Alkali metal fluorides supported on silica gel or large pore molecular sieves gave much weaker colours and σ-complexes were only detectable by ^1H n.m.r. after prolonged heating.

TABLE

^{1}H and ^{19}F N.m.r. Resonances[1] of 1-Chloro-2,4-dinitrobenzene, 1-Fluoro-2,4-dinitrobenzene and their Complexes with F^{-2}

	1-Chloro-2,4-dinitrobenzene			1-Fluoro-2,4-dinitrobenzene		
	Parent	Complex	Δ[3]	Parent	Complex	Δ[3]
H_3	8.95 (d)	8.50(d)	0.45	8.88 (d of d)	8.55(d)	0.33
H_5	8.55 (d of d)	7.70 (d of d)	0.85	8.70 (d of d)	7.80 (d of d)	0.90
H_6	8.15(d)	6.30(d)	1.85	7.95 (d of d)	6.35(d)	1.60
F	-	-54 (s,br)	-	-107 (mult.)	-54 (s,br)	53



[1] p.p.m. with respect to TMS (^{1}H) and $CFCl_3$ (^{19}F).

[2] For comparison purposes the hydrogens in all species are labelled in the same way.

[3] δ(parent) - δ(complex).

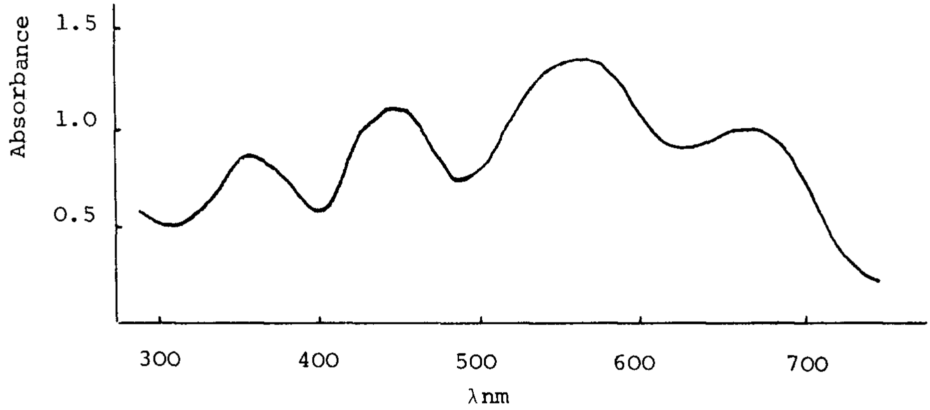


Fig. 3. Spectrum of a fresh solution of meta-dinitrobenzene in DMSO (0.00001M) containing Bu_4NF (ca.0.00005M equiv. F^-) in a 10 mm cell. S ^{4} similar spectrum can be obtained using KF-alumina at 50°C although all of the bands and especially those at 680 and 570 nm are less intense.

It is apparent from comparison of our results with other studies of Meisenheimer complexes [6] that the use of supported salts or "anhydrous" quaternary ammonium salts may allow the study of complexes of relatively weak electrophiles. For the fluoro-complexes studied here, the observed ease of formation follows the order $Bu^n{}_4NF$>CsF-alumina>KF-silica, KF-molecular sieves, CsF, KF-18-crown-6>KF. The enhanced reactivity of the supported salts compared to unsupported salts is consistent with other studies [3,5,9-11] as is the observation that alumina is the best support material for fluorides [9]. Presumably the stronger cation coordinating ability and weaker anion coordinating ability of the surface hydroxyls of alumina compared to those on silica gel result in a more labile F^- source. The relative inefficiency of KF-18-crown-6 is perhaps surprising when one considers the successful use of this reagent in preparing fluorotrinitrobenzene complexes [2] and in converting 1-chloro-2,4-dinitrobenzene to 1-fluoro-2,4-dinitrobenzene [12]. It is known that ion-pairing can play an important role in the stabilisation of Meisenheimer complexes [13] and it may be that a poor interaction between the complex anion of a dinitrobenzene and the fairly "soft" crown complexed potassium cation makes the complex unstable towards decomposition (to product or to starting material).

EXPERIMENTAL

All inorganic reagents were BDH materials and were dried before use. The supported fluorides were prepared by slow evaporation with thorough mixing of mixtures of the fluoride (20 mmole) and neutral alumina (10 g) in water (100 cm^3) to give a loading of 2 mmole F^-/g alumina which is approximately equivalent to a monolayer coverage [3]. The resulting solids were dried at temperatures up to 50°C in vacuo. Tetra-n-butylammonium fluoride can be prepared from the hydroxide by neutralisation to pH 7-8 with dilute aqueous HF. The resulting solution was concentrated to a solid trihydrate by repeated evaporation from excess acetonitrile and then further concentrated to $Bu^n{}_4NF$. ca. $0.5H_2O$ (an oil) by heating at 50-60°C at 0.2 mmHg for 24h. Solvents were routinely dried with molecular sieves or calcium hydride before use. The aromatic compounds were commercial reagents used without further treatment.

The σ-complexes were usually generated by stirring a concentrated solution of the aromatic with the F^- reagent (3-5 mole equivalents of the fluoride were routinely used and 10 mole equivalents of the fluoride were used for reactions requiring a large excess of F^-). Samples of the supernatant were removed and diluted to $<10^{-4}$ molar of the aromatic for electronic absorption spectroscopy or were used neat for n.m.r. spectroscopy. Once equilibrium was established, solutions of the more stable σ-complex appeared to be stable over a period of at least several days in the systems employing supported alkali metal fluorides. The product 1-fluoro-2,4-dinitrobenzene was isolated from the reaction mixture by repeated extraction with ether followed by water washing and evaporation to dryness.

^{1}H N.m.r. spectra were recorded using a Varian EM360A (60 MHz) spectrometer. ^{19}F N.m.r. spectra were recorded using a Jeol FX90Q spectrometer operating at 84.67 MHz or a Bruker WP80 spectrometer operating at 75.26 MHz. Visible spectra were recorded using a Varian 2300 u.v.-vis.-near i.r. spectrophotometer.

ACKNOWLEDGEMENT

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