A Study of Transient Species formed during Aromatic Nitrosodeiodination

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Intense, transient colours are produced during the nitrosation of a number of aromatic compounds. The spectrum of that obtained from 4-iodoanisole has been determined by stopped-flow spectrophotometry. The kinetics of the formation of the coloured species from 2-(4-iodophenoxy)ethanesulphonic acid in aqueous solution have been examined. It is concluded that the coloured species are σ-complexes.

THE reaction of 4-iodoanisole with nitric acid and sodium nitrite in acetic acid solution results, *inter alia*, in replacement of the iodine atom by a nitroso-group and subsequent oxidation to the nitro-compound. The detailed mechanism of this reaction has been reported,[1] but one observation, the formation of a transient yellow species immediately on mixing, was only mentioned in passing. A more detailed study of this aspect of the reaction is now described.

RESULTS AND DISCUSSION

The colour resulting from mixing the reactants disappears almost completely within 30 s and thus is not susceptible to study by conventional spectroscopy. However, spectral changes occurring during the first minute after mixing can be examined by stopped-flow spectrophotometry. These changes were examined at various wavelengths between 380 and 490 nm and a typical run is shown in Figure 1. In all cases the absorbance reached a maximum 10 s after mixing and this was taken to be the time at which the species responsible for the colour was at maximum concentration. Absorbance values after 10 s at various wavelengths are given in the Table. These represent the spectrum of the transient species, which is a broad band with a maximum below 380 nm. Unfortunately, owing to instrumental limitations, it was not possible to observe changes at lower wavelengths. The spectrum obtained contains no distinctive features and did not help to identify the

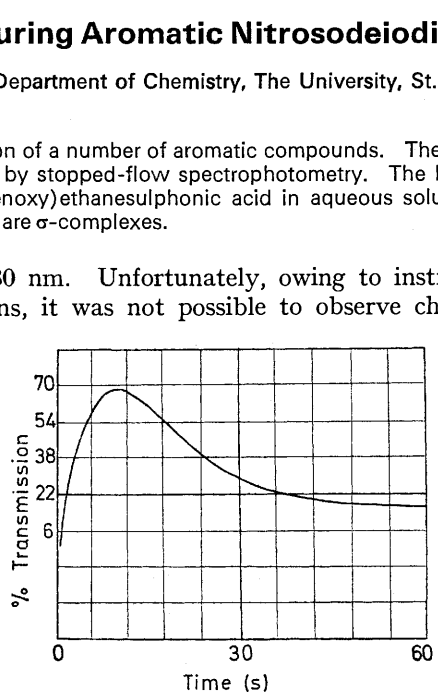

FIGURE 1 Variation of absorbance at 420 nm with time in the nitrosodeiodination of 4-iodoanisole

Absorbance of the transient species formed during nitrosodeiodination of 4-iodoanisole in acetic acid 10 s after mixing at 25°

$[HNO_3] = 8{\cdot}05\text{M}$ $[NaNO_2] = 0{\cdot}025\text{M}$

$[\text{4-iodoanisole}] = 5{\cdot}22 \times 10^{-3}\text{M}$

λ/nm	380	400	420	440	460	475	490
Absorbance	0·56	0·54	0·53	0·48	0·34	0·12	0·08

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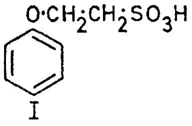
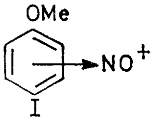
[1] A. R. Butler and A. P. Sanderson, *J. Chem. Soc.* (*B*), 1971, 2264.

species responsible. Replacement of 4-iodoanisole by 2,4-di-iodoanisole or 4-iodo-2-nitroanisole, which also undergo nitrosodeiodination, did not result in the formation of any transient species with a visible spectrum.

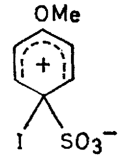
The reagent mixture used in the preceding study is complex, and it was thought that use of a simpler one (acidified aqueous nitrous acid) would assist further study of nitrosodeiodination. For this a water-soluble substrate was required, and 2-(4-iodophenoxy)ethanesulphonic acid (I) was selected and prepared. Addition of this material to sodium nitrite in perchloric acid resulted in the slow formation of an intense brown colour which eventually disappeared; the resulting solution was faintly yellow. The spectrum of the final solution was qualitatively and quantitatively as expected for the presence of iodine resulting from the complete deiodination of (I). Addition of alkali produced a yellow solution with a spectrum characterstic of the 4-nitrophenolate ion, indicating that dealkylation had accompanied nitrosodeiodination. This behaviour parallels that of anisole itself, where nitrosation gives 4-nitrophenol and ether cleavage occurs after nitrosation.[2] The initial intense colour was assumed to be due to the same type of species as that observed with 4-iodoanisole and, because of the simpler reaction conditions, we were able to examine its formation in detail.



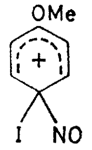
(I)



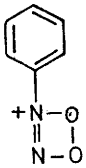
(II)



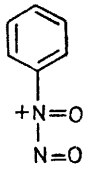
(III)



(IV)



(V)



(VII)

The maximum absorption occurred at 410 nm and a plot of optical density at 410 nm against time gave a curve with a shape similar to that in Figure 1, but with a time scale in minutes rather than seconds. By adjustment of the concentrations of reactants it was possible to make the disappearance of the colour slow enough for the kinetics of its appearance to be examined without complicated computations. The formation of the species responsible for the colour was found to conform to first-order kinetics over at least three half-lives. The rate of formation was directly proportional to the sodium nitrite concentration (Figure 2) and to the acidity as represented by the acidity function H_R (Figure 3).

The linear dependence upon the sodium nitrite concentration indicates that the reaction under consideration is nitrosation or a closely related reaction, and the variation of rate with acidity is consistent with this. The slope of the line in Figure 3 is 0·38, which is very different from that found by Challis and Lawson [2] for the acidity dependance of the nitrosation of anisole, but, as these authors point out,[3] the slope of such a line is not diagnostic unless the rate-determining step is known. The nitrosating species NO^+ is known to exist in perchloric acid and its concentration in equilibrium with molecular nitrous acid parallels the h_R acidity function,[4] so that the linear relationship of Figure 3 is not without significance.

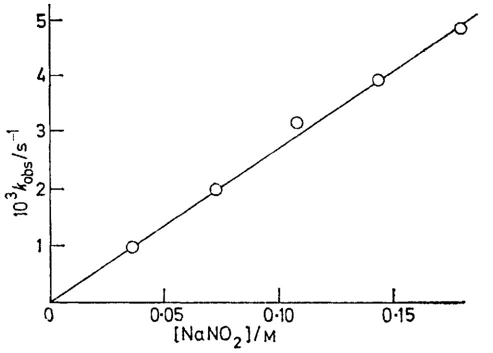


FIGURE 2 Variation of k_{obs} with $[NaNO_2]$ for formation of the brown species in the nitrosodeiodination of 2-(4-iodophenoxy)-ethanesulphonic acid at 25°; [substrate] = $2{\cdot}76 \times 10^{-3}M$; $[HClO_4] = 6{\cdot}48M$

The structure of the species responsible for the colour must now be considered. A similar colour was found when 2-phenoxyethanesulphonic acid was used as substrate, and so the presence of an iodo-group is not essential. The kinetic evidence suggests that formation of the colour requires a nitrosating species and it is tempting, therefore, to believe that the species is an intermediate on the pathway of aromatic nitrosation. The most obvious choice is a π-complex (II),[5] and such complexes have been suggested as responsible for the colour result-

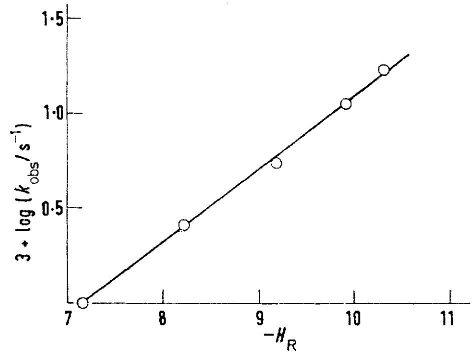


FIGURE 3 Variation of log k_{obs} with acidity of perchloric acid for formation of the brown species in the nitrosodeiodination of 2-(4-iodophenoxy)ethanesulphonic acid at 25°; [substrate] = $2{\cdot}76 \times 10^{-3}M$; $[NaNO_2] = 0{\cdot}041M$

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[2] B. C. Challis and A. J. Lawson, *J. Chem. Soc.* (*B*), 1971, 770.

[3] B. C. Challis and A. J. Lawson, *Chem. Comm.*, 1968, 818.

[4] K. Singer and P. A. Vamplew, *J. Chem. Soc.*, 1956, 3971.

[5] D. V. Banthorpe, *Chem. Rev.*, 1970, **70**, 295.

ing from the interaction of nitrosylsulphuric acid with various aromatic compounds.[6] Further support comes from our observation that, although hexamethylbenzene is insoluble in perchloric acid, addition of sodium nitrite effects dissolution and a brown colour is produced. Hexamethylbenzene is recovered unchanged from the solution by addition of urea, which destroys the nitrous acid. Hexaethylbenzene does not react and is known to be unable to form π-complexes for steric reasons.[7] However, there is one compelling piece of evidence against the colour being due to a π-complex: the formation of such a complex, involving only electron transfer, cannot be as slow a process as that observed in this study. Therefore, in spite of evidence in its favour, we reject this possibility.

A second possible intermediate on the pathway to nitrosation is a σ-complex. A brown solution is formed on addition of 2- or 4-iodoanisole to concentrated sulphuric acid (the Jacobsen reaction) and this has been ascribed to the σ-complex (III),[8] so the suggestion is not without precedent. However, there is some doubt about the colour of a σ-complex. In a detailed spectral study Hunziker, Penton, and Zollinger[9] conclude that the colour resulting from the reaction of nitrosonium hexafluorophosphate and pentamethylbenzene is not due to a σ-complex. However, methylbenzenium tetrafluoroborates (where the cation is the protonated methylbenzene) are coloured,[10] and the σ-complex resulting from the bromination of tris(dimethylamino)benzene (which can be isolated) is deep red in solution.[11] We believe, therefore, that identifying the colour as due to the σ-complex (IV) is consistent with the available data, both spectroscopic and kinetic.

The possibility that the transient species is not on the pathway of aromatic nitrosation must be considered. The shape of the curve in Figure 1 is typical[12] of an intermediate (B) in a reaction sequence (A) → (B) → (C) and it is partly because of this that we propose (IV) as the structure of (B). However, studies with an analogue computer (details on request) indicate that the kinetics are equally consistent with the reaction sequence (B) ⇌ (A) → (C), where (B) is again responsible for the colour but is not on the reaction path [*i.e.* (A) → (C)]. Although we have obtained the spectrum of one of the coloured species we could not, owing to its transient nature, measure the molar extinction coefficient, and so the colour could be due to the presence of a very low concentration of a species with a high absorbance. In this sense it could be the result of an unimportant side reaction. Transient colour formation in aromatic nitration is a common observation and it was established by Benford and Ingold[13] that this occurs only in the presence of nitrous acid. Later Ingold and his co-workers[14] suggested that the colour obtained during the nitration of anisole in nitromethane is due to dianisylaminyl oxide. However, the appearance of the brown colour under a variety of conditions in the present work, and also in the Jacobsen reaction,[8] make a σ-complex more likely than a species related to that suggested by Ingold[14] for a reaction occurring under non-aqueous conditions.

Certain activated aromatic compounds form diazonium salts on nitrosation.[15] This process involves nitrosation, followed by reaction with more nitrous acid. A brown intermediate is formed during the second of these reactions, for which structures (V) and (VI) were proposed by Tedder and Theaker.[16] It is possible that similar species are formed after nitrosodeiodination. The reaction between nitrous acid and (I) was allowed to proceed to completion (*i.e.* such that no colour apart from that of iodine remained), and alkaline β-naphthol was added. No colour resulted, indicating the absence of any diazonium compound; structures analogous to (V) and (VI) are, therefore, unlikely to be responsible for the colour occurring during nitrosodeiodination. In the light of all these considerations, we consider that the brown intermediates observed in this study are most likely to be σ-complexes of type (IV).

EXPERIMENTAL

Materials.—4-Iodoanisole, hexamethylbenzene, and hexaethylbenzene were recrystallised from ethanol before use. Syntheses of 2,4-di-iodoanisole and 4-iodo-2-nitroanisole have been described previously.[1]

A solution of 4-iodophenol[17] (40 g) in ethanol (500 ml) was refluxed for 4 h with 1,2-dibromoethane (40 ml) and sodium (5 g). The mixture was poured into water and the white precipitate of 1-bromo-2-(4-iodophenoxy)ethane was filtered off (17·8 g, 30%). A solution of this compound (10 g) and sodium sulphite heptahydrate (8 g) in water (15 ml) was refluxed for 30 h. The white precipitate was filtered off and crystallised from ethanol and then water to give *sodium* 2-(4-*iodophenoxy*)*ethanesulphonate* (1·3 g, 15%) (Found: C, 27·3; H, 2·3. $C_8H_8INaO_4$ requires C, 26·45; H, 2·3%). Sodium 2-phenoxyethanesulphonate was prepared in a similar manner.[18]

Kinetic Methods.—For the study of the nitrosodeiodination of 4-iodoanisole a mixture of acetic and nitric acid was contained in one reservoir of a Canterbury stopped-flow spectrophotometer and a solution of sodium nitrite and

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4-iodoanisole in acetic acid in the other. After mixing, the signal from the photomultiplier was displayed on an Advance OS300 oscilloscope and photographed. The response of the photomultiplier was calibrated at each wavelength by the use of solutions of known optical density.

The reactions of 2-(4-iodophenoxy)ethanesulphonic acid and 2-phenoxyethane sulphonic acid were monitored at 410 nm with a Unicam SP 500 spectrophotometer.

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