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STUDIES ON THE TWO-PHASE NITRATION OF PHENOLS (part 2)

Malcolm J. Thompson and Petrus J. Zeegers*

School of Physical Sciences
The Flinders University of South Australia
Bedford Park S.A. 5042
AUSTRALIA

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Abstract: Gas phase Ionization Potentials can be correlated with solution Oxidation Potentials for phenols and used to predict the likelihood of successful nitration using the two-phase procedure. The interaction of steric and electronic effects then determines the sites of nitration by radical recombination of the phenoxy radical and NO_2. Nitration of dioxybenzenes may give insights into the nitration mechanism

INTRODUCTION

In our earlier report[1] we proposed that the two-phase nitration of phenols was initiated by an electron transfer reaction (ET) between the aromatic and NO^+. Loss of a proton from the subsequent radical cation leads to a phenoxy radical, in which the single electron spin density determines the product distribution. We would now like to present evidence that the gas phase Ionization Potential (IP) as determined by (SCF) MO calculation for various phenolic compounds can be correlated with experimentally determined oxidation potentials ($E_{1/2}$). Furthermore the IP values can be used as a predictor in determining whether or not nitration will proceed for a particular phenol. We have also extended our study to include a range of 3-substituted phenols in order to determine whether we can predict the product isomer ratios for the nitration of phenols containing substituents other than alkyl groups. In particular we were interested in the interaction of electronic and steric effects of strongly electron withdrawing groups. We have investigated the electronic influence of eight electron withdrawing groups with σ_I values ranging from 0.25(OH) to 0.65(NO_2). We compared the predicted isomer ratio as determined by the spin density of the unpaired electron in the SOMO of the phenoxy radical, to those determined by GLC and/or ^{1}H-NMR analysis of the total product of the reaction. We also wished to explore the limits of this reaction in terms of its synthetic viability when strong deactivating groups are present and whether we could predict the limits of the reaction by using the calculated gas-phase Ionization Potential. Finally we investigated the nitration reaction in a series of dioxy-benzenes as a means of confirming the intermediacy of a phenoxy radical in the nitration mechanism as previously proposed. As we had previously noted the failure of methoxybenzene (anisole) to nitrate by the two-phase procedure , we wished to see if dimethoxybenzenes, compounds with a favourably low IP and $E_{1/2}$, would also fail to nitrate.

RESULTS

The gas phase Ionization Potentials were calculated using the AM1 Hamiltonian operator of the semi empirical MO method available through the QCPE[11]. All parameters were free to optimize with no restrictions. The reference phenols which were chosen for our MO studies have had their oxidation potentials measured by cyclic voltametry and were readily available compounds. Table 1 lists the phenols which were subjected to the two-phase nitration, with the calculated IP values and the experimental $E_{1/2}$ values. The first 20 compounds listed are those used to determine the correlation between IP and $E_{1/2}$. The $E_{1/2}$ values were recorded by Suatoni et al[5] in 50% isopropanol : acetate buffer at pH=5.6. A SCE was used as the reference and a graphite electrode as the polarizing electrode. The other values were extrapolated from other sources [5-7]. Previous workers [2-4] have correlated the IP and $E_{1/2}$ values of aromatic hydrocarbons and and have generally found good linear correlations. Figure 1 is a plot of IP vs $E_{1/2}$ for the 20 reference compounds. We obtained a satisfactory straight line with a correlation coefficient of $R = 0.96$ for the relationship

$$E_{1/2} = 0.33\ \mathrm{IP} - 2.43$$

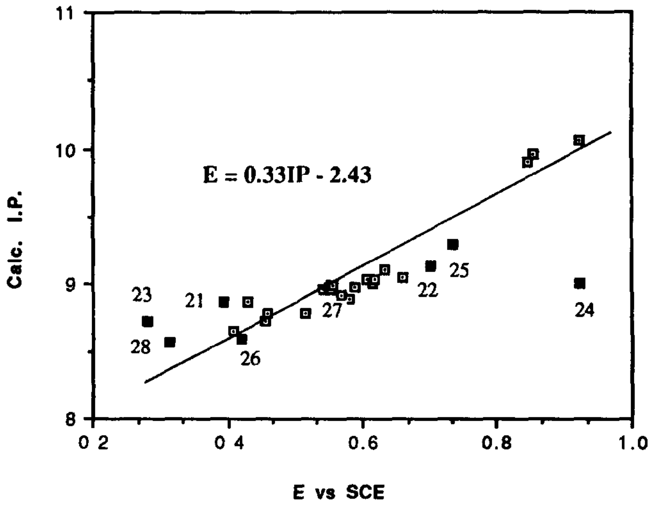
Compounds 21-28 though not included in this correlation were also nitrated and are shown separately on the graph. Our observation would suggest that phenolic compounds with an $IP > 10.0$ and/or falling well below our linear plot will nitrate very slowly (if at all.) Conversely those compounds with an $IP < 9.0$ and a lower than expected $E_{1/2}$ value appear to be prone to formation of oxidation products such as quinones or destructive oxidation type products. Our calculations for the compounds which are readily oxidized, show that the phenoxy radical intermediate has an $IP < 10$. It is thus feasible that a second oxidation of the radical can occur, with NO^+ or HNO_3 as oxidant, to form the corresponding cation. This in turn is suscepible to solvolysis , leading to the formation of hydroquinones, oxidation of which gives quinones.

Miller et al [2] have previously commented on the lower than expected value for $E_{1/2}$ for phenol due to special solvation in basic media. By using the values found by Suatoni in an acidic medium and comparing only compounds of a similar nature we believe that solvation effects should be fairly constant. The exceptions would be

Table 1

	PHENOL	Cal.IP(eV)	E vs SCE(V)	Reference
1	PHENOL	9.11	0.633	5
2	o-METHYL	8.99	0.556	5
3	m-METHYL	9.03	0.607	5
4	p-METHYL	8.99	0.554	5
5	o-ETHYL	8.98	0.551	5
6	m-ETHYL	9.01	0.616	5
7	p-ETHYL	8.92	0.567	5
8	o-tBUTYL	8.96	0.552	5
9	p-tBUTYL	8.98	0.578	5
10	2,4-DIMETHYL	8.78	0.459	5
11	2,6-DIMETHYL	8.88	0.427	5
12	3,4-DIMETHYL	8.79	0.513	5
13	3,5-DIMETHYL	8.97	0.587	5
14	o-NITRO	9.91	0.846	5
15	m-NITRO	9.96	0.855	5
16	p-NITRO	10.07	0.924	5
17	o-METHOXY	8.73	0.456	5
18	m-METHOXY	9.04	0.619	5
19	p-METHOXY	8.65	0.406	5
20	m-CHLORO	9.29	0.734	5
21	o-HYDROXY	8.88	0.394	6
22	m-HYDROXY	9.05	0.658	6
23	p-HYDROXY	8.73	0.279	6
24	ANISOLE	9.00	0.923	7
25	VANILLIN	9.13	0.700	5
26	1,2-DMB	8.59	0.420	7
27	1,3-DMB	8.96	0.540	7
28	1,4-DMB	8.57	0.313	7
29	m-FLUORO	9.32		
30	m-CYANO	9.57		
31	m-CHO	9.44		
32	m-COCH$_3$	9.38		

Figure 1 Plot of calc IP (eV) vs E (V)



those compounds with no phenoxy proton, eg phenolic ethers. For these compounds the solvation effect would be expected to be different. Anisole itself correlates poorly with our linear plot and thus its failure to nitrate is not unexpected.

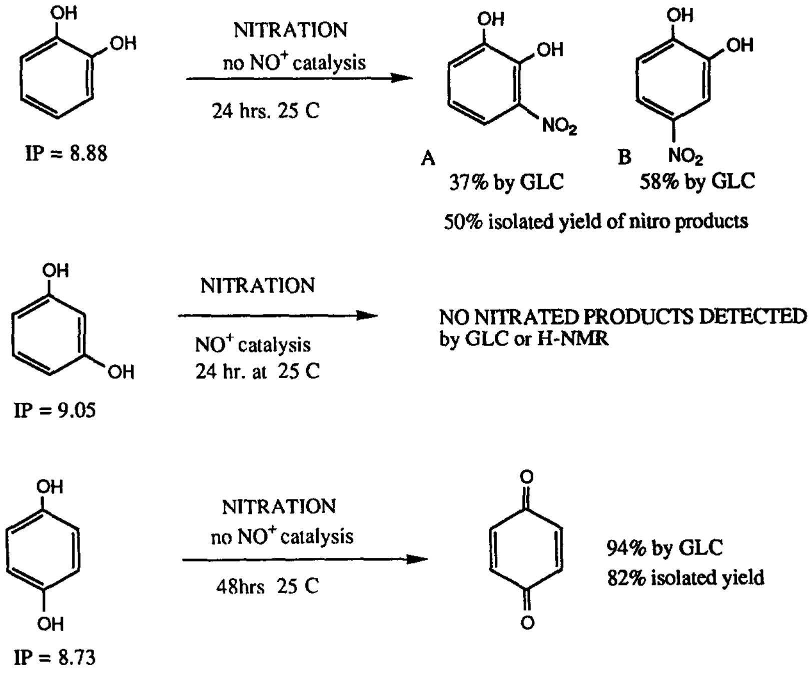
As both the IP and $E_{1/2}$ values correlate with the energy of the HOMO it would be expected that those compounds with an IP lower than phenol (IP=9.11) should nitrate faster than phenol. The converse is also expected to be true. This is what we have observed to be the case, with several notable exceptions. As reported earlier anisole did not nitrate by this procedure. We proposed that its behaviour results from its reluctance to form a phenoxy radical. If this were the case then a similar argument should hold for dimethoxybenzenes. The dioxybenzenes proved to be an interesting group of compounds and their nitration will be discussed in some detail.

Nitration of Dioxybenzenes

The three dihydroxybenzenes (DHB) showed considerable variation toward nitration. 1,2 DHB (IP= 8.88) underwent nitration to give 2 main nitro products as shown in fig.2. In the presence of NO^+ catalysis the reaction was very rapid, but gave a considerable amount of tarry product. The behaviour of 1,2-DHB toward the nitration procedure could be reasoned to be a result of its lower than predicted $E_{1/2}$ value in solution. This would make it prone to oxidation.

Figure 2

THE TWO-PHASE NITRATION OF DIHYDROXYBENZENES



A similar pattern of behaviour would be predicted for 1,4-DHB (IP=8.73). In this case however the main product observed was 1,4-benzoquinone. No nitrated products were detected by GLC. Product isolation confirmed this, as only quinone and starting material were recovered. The behaviour of 1,3-DHB(IP=9.05) is difficult to rationalize. With an IP and $E_{1/2}$ comparable to that of of phenol we expected it to nitrate readily. All attempts to nitrate it were unsuccessful.

During the attempted nitration of 1,3-DHB an initial faint orange colour developed after several minutes. This colour deepened over the next 48 hours to an intense red/violet. The total reaction mixture showed the presence of several small coloured spots by TLC. GLC and H-NMR showed only starting material. Product isolation after chromatography yielded only 65% of the starting material, no other identifiable product was isolated. At this stage we can offer no plausible explanation for its reluctance to nitrate by the two-phase procedure.

Elving and Krivis [6] have noted the anomalous behavior of 1,3-DHB compared with its isomers(1,2-DHB and 1,4-DHB) in oxidative voltametry experiments. The authors observed it had a considerably higher $E_{1/2}$ value with a much lower than expected current. They concluded that the 1,3-DHB compound underwent a different type of oxidation reaction, but did not elaborate on their finding.

Nitration of each of the methoxyphenols proceeded rapidly in the presence of NO^+ catalysis with good yields of isolated products. Formation of tarry products decreased the isolated yield for 3-methoxyphenol. The yield of this reaction could be enhanced in the absence of NO^+ catalysis but at the expense of longer reaction time. As predicted from the IP values each nitrated faster than phenol. The hydroxy group, via its radical is the primary directive group for product formation. Figure 3 gives a summary of the products found.

The rate of nitration of the dimethoxybenzenes (DMB) was considerably slower than for phenol despite lower values for IP and $E_{1/2}$. Figure 4 gives a summary of the products found. Both 1,2-DMB and 1,4-DMB gave a single mono-nitrated product. Allan and Robinson[8] using nitric acid-acetic acid as the nitrating medium, have also observed a single product for the nitration of 1,2-DHB. This result could be interpreted as indicating a nitrosation-oxidation mechanism. Alternatively it could involve nitration of a radical cation formed by initial ET reaction. MO calculations show that the spins in the radical cation are higher at the 4 and 5 positions (0.1300) than at the 3 and 6 positions (0.0046). Radical recombination between the radical cation and NO_2 is favoured at those positions having higher spin.

1,3-DMB was the slowest of the three isomers to undergo nitration. The products are shown in fig.4 The main product was 4-nitro-3-methoxyphenol resulting from demethylation. Comparison with the nitration products from 3-methoxyphenol suggests a different mechanism and that the demethylation occurs after nitration

Figure 3

NITRATION OF METHOXYPHENOLS

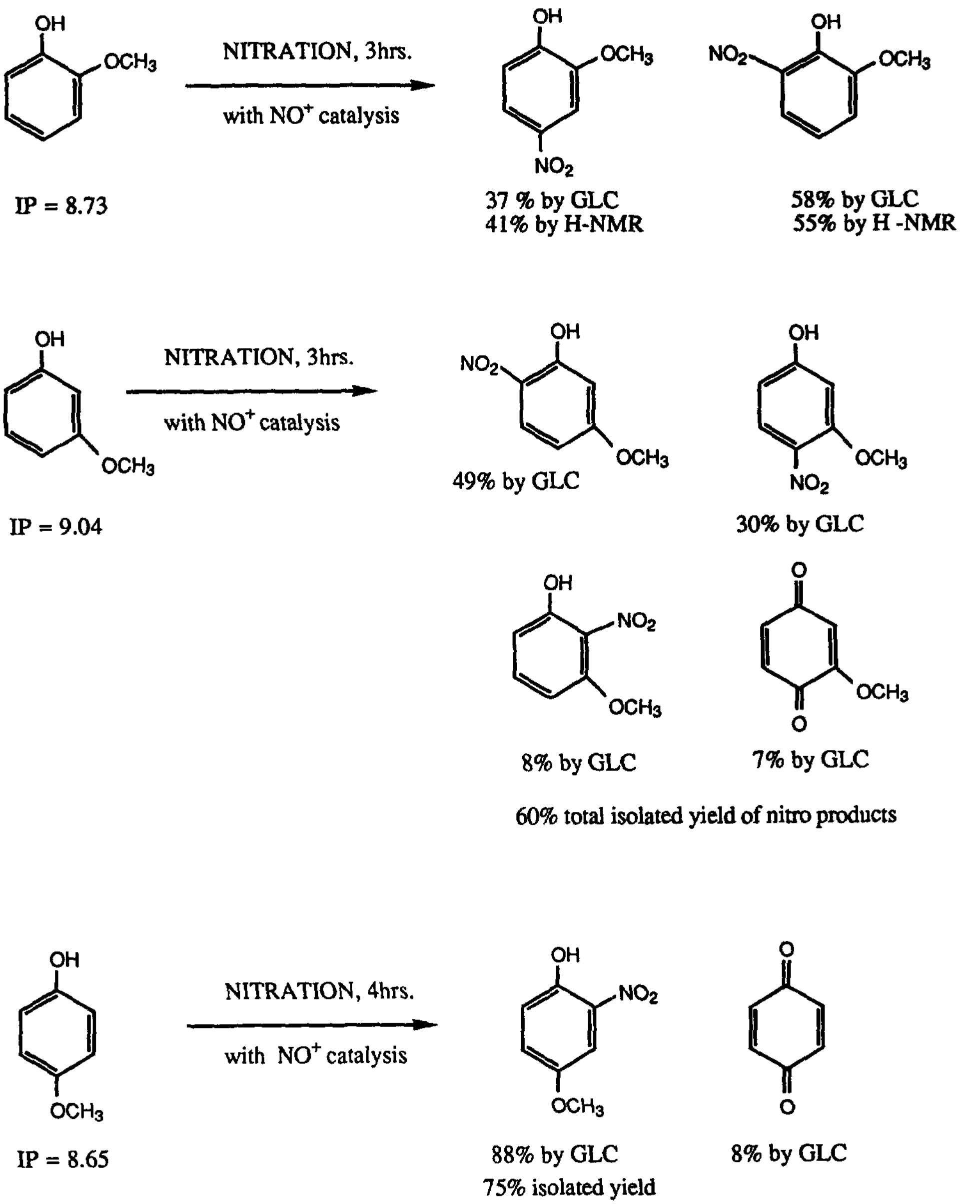
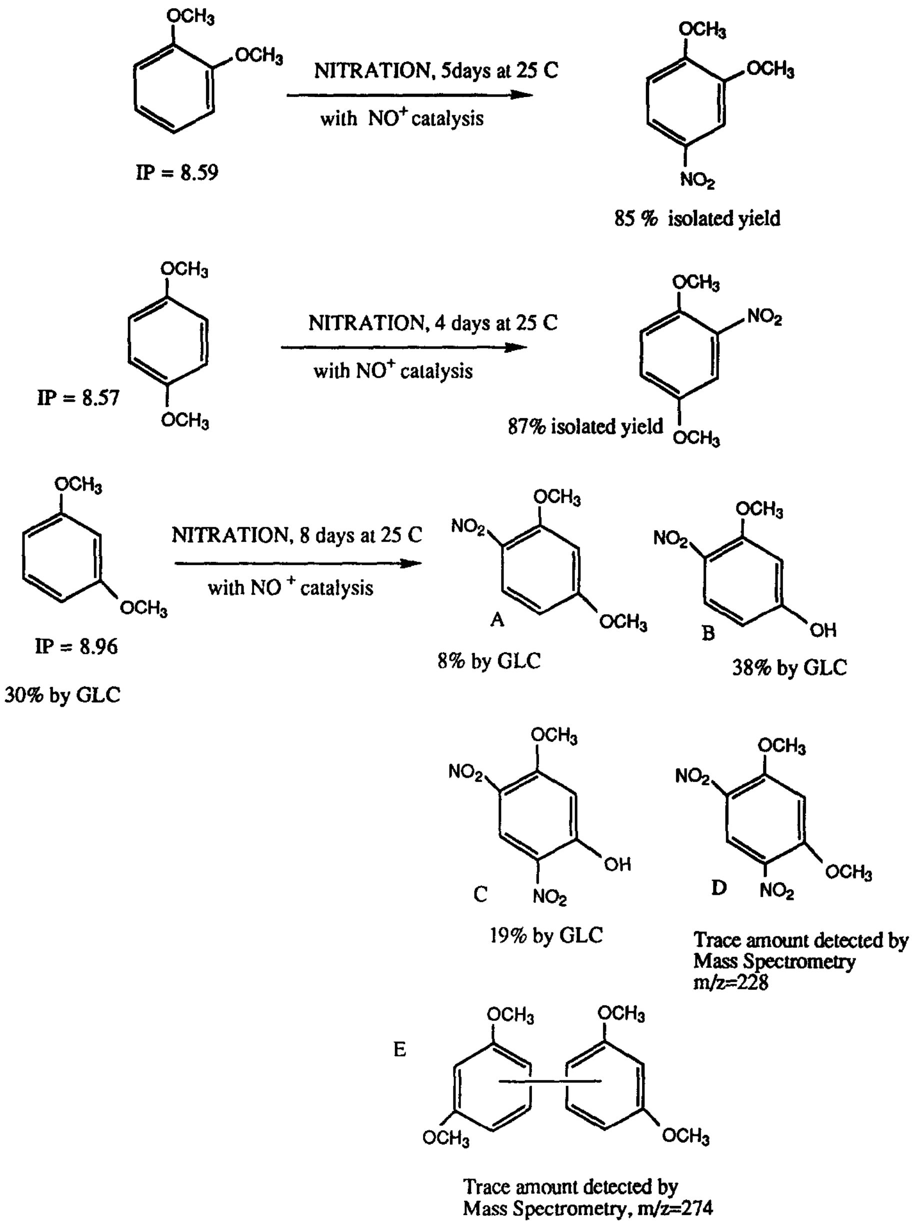


Figure 4

NITRATION OF DIMETHOXYBENZENES



at the methoxy group para to the nitro. If demethylation occurs prior to nitration the product ratio should be identical to that found for nitration of 3-methoxyphenol (see fig 3). Kochi et al [10] nitrated 1,3 -DMB with nitric acid/acetic acid and found the main product to be 2,4-dimethoxynitrobenzene. They proposed that the intermediate leading to electrophilic nitration is the same as that involved in charge transfer nitration, namely the radical cation. Nitration then procedes via the radical pair, $R^{\bullet +}$ and NO_2. It is feasible that the first formed product in our reaction is also 2,4-dimethoxy-nitrobenzene and that the other nitro products are derived from it by further reaction. Formation of the dinitro product (C) in the presence of considerable starting material was also unexpected. It could be rationalized by demethylation of A to give B. This being a phenol, should be more active to further nitration than either compound A or 1,3-DMB. Kochi detected by mass spectrometry but did not isolate a product believed to be a tetramethoxydiphenyl. In the total nitration product of our procedure we have also observed by mass spectrometer an ion with m/z=274, suggesting the presence of the diphenyl product.

Nitration of 3-substituted phenols

We have previously shown that the product distribution of the nitration reaction can be determined by the unpaired spin density of the phenoxy radical. This procedure has to date only been tried with alkyl groups and it was evident that this becomes less accurate as the substituent group becomes larger. This may simply reflect the inability of the MO program to account for steric effects. We now wish to report our findings for eight electron withdrawing groups and include the alkyl groups for comparison.

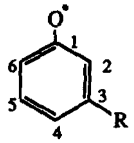
Table 2 shows the calculated spin density for all the 3-substituted compounds. The substituents in compounds 2-4 are electron donating alkyl groups and compounds 5-12 have electron withdrawing substituents. For the electron withdrawing groups (5-12) there are two subgroups. Compounds 5-8 contain groups which are electron withdrawing inductively (-I) but can donate electrons mesomerically(+M). Compounds 9-12 all have strong electron withdrawing groups (-I,-M). In general the MO program predicts that the para quinoid form of the radical intermediate is the most stable form and thus we would expect the 4-nitro compound to be the predominant nitration product.

Groups 5-8 appear to have the greatest influence on the spin density distribution. In particular there was a marked reduction in spin density at the 2-position with a concomitant increase at the 6-position The largest difference was observed for 1,3-DHB(entry 5) but as mentioned previously it failed to nitrate. Based on these spin density calculations we expected to find a reduction in the relative amount of the 2-nitro product and an increase in the 6-nitro product for each of the compounds 6-8. Tables 3 and 4 show that the calculated product ratios and those determined experimentally are in reasonable agreement.

Table 2

PHENOXY RADICALS

Unpaired electron spin density of phenoxy radicals using AM1 SCF (UHF) method by taking the square of the SOMO coefficient, $(c_i)^2$



		C-1	C-2	C-3	C-4	C-5	C-6	O
1	R = H	0.0322	0.2199	0.0043	0.3847	0.0042	0.2208	0.1338
2	R = Me	0.0314	0.1972	0.0049	0.3950	0.0038	0.2387	0.1310
3	R = Eth	0.0302	0.1978	0.0049	0.3936	0.0042	0.2336	0.1311
4	R = tBu	0.0322	0.1987	0.0043	0.3950	0.0048	0.2304	0.1306
5	R = OH	0.0255	0.1109	0.0089	0.4163	0.0010	0.3058	0.1190
6	R = MeO	0.0284	0.1639	0.0048	0.3959	0.0009	0.2697	0.1312
7	R = F	0.0274	0.1482	0.0079	0.3974	0.0008	0.2847	0.1288
8	R = Cl	0.0291	0.1680	0.0074	0.3971	0.0016	0.2607	0.1286
9	R = CN	0.0314	0.1939	0.0079	0.3853	0.0022	0.2432	0.1328
10	R = NO_2	0.0318	0.2133	0.0082	0.3733	0.0022	0.2339	0.1361
11	R = CHO	0.0340	0.2028	0.0108	0.3852	0.0038	0.2297	0.1314
12	R = COMe	0.0339	0.1993	0.0105	0.3877	0.0042	0.2304	0.1302

In each case the amount of the 2-nitro product has been reduced by comparison to the reference compound (phenol). Similarly there has been an increase in the 6-nitro product. We propose that this is due primarily to the electronic influence of the substituent group on the distribution of the odd electron in the phenoxy radical. This effect is most evident in compounds 5-8. For the case of the fluoro and methoxy substituents the product distribution does not fit the general pattern of the other compounds. This is highlighted by the considerable difference in the 1/2 o:p ratio compared to the other compounds. For these two compounds (-I,+M) we have found the predominant product of nitration to be the 6-nitro isomer (2-nitro-5-fluorophenol and 2-nitro-5-methoxyphenol respectively) . MO calculations predict that there would be an increase in the amount of the 6-nitro product at the expense of the 2-nitro, based on the electronic perturbation of the substituent group.

Table 3

Nitration product distribution of 3-substituted phenols as predicted by the unpaired spin density of the SOMO

R	2-Nitro	4-Nitro	6-Nitro	1/2 o:p ratio
1. H	26.6	46.6	26.6	0.57
2. Me	23.3	47.8	28.9	0.55
3. Eth	23.9	47.7	28.3	0.55
4. tBu	24.1	47.9	28.0	0.54
5. OH	12.8	47.9	35.2	0.50
6. OMe	18.9	45.8	31.2	0.55
7. F	17.1	45.9	32.9	0.54
8. Cl	19.5	45.9	30.2	0.54
9. CN	22.4	44.6	28.1	0.57
10. CHO	23.4	44.5	26.5	0.56
11. COMe	23.0	44.8	26.6	0.55
12. NO_2	24.7	43.3	27.1	0.60

Table 4

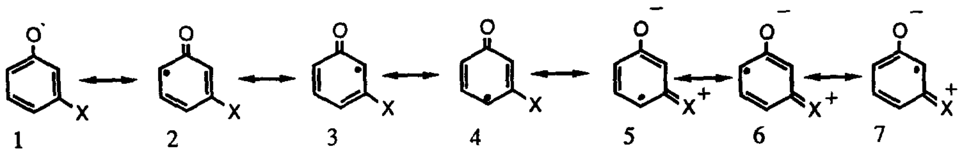
Nitration product distribution of 3-substituted phenols as determined by GLC and/or H-NMR as % of total product.

R	2-Nitro	4-Nitro	6-Nitro	Total	1/2 o:p
1. H	27.5	41.3	27.5	96.3	0.66
2. Me	22.5	41.0	27.9	91.4	0.62
3. Eth	20.5	41.4	29.9	91.8	0.61
4. tBu	19.3	40.7	34.8	94.5	0.66
5. OH*	----	----	----	----	----
6. OMe	8.0	30.0	49.0	87.0	0.95
7. F*	17.0	31.0	37.8	85.8	0.88
8. Cl*	20.2	34.7	28.7	83.6	0.70
9. CN*	22.0	32.5	22.9	77.4	0.69
10. CHO*	22.6	38.4	25.2	86.0	0.62
11. COMe*	24.9	40.3	28.7	93.9	0.66
12. NO_2*	8.5	21.0	17.4	46.9	0.62

NOTES

(a) all reactions were done at 25C for 24 hours unless stated otherwise
(b) 1,2,3,4,5,6,7,8,11 were determined by GLC of the total nitration product
(c) 5,9,10,12 were determined by GLC of the methyl ether after methylation with diazomethane
(d) 6,10,11 were also determined by H-NMR of the total product
(e) in the following reactions* nitration was incomplete, as indicated by the presence of starting material even after extended reaction time, up to 3 days in the case of reactions 9,10,11 and 5 days for reactions 5 and 12
(f) for all reactions the product ratio was confirmed by product isolation using silica gel chromatography.

In order to account for the product distribution for compounds 5-8 we suggest that the substituent group acts as a pi- donor (+M). This leads to the possibility of 7 canonical forms shown below, including the ionic forms (structures 5-7)



If we consider the radical centre in the aromatic ring(structures 2-4) to be electron deficient in nature then the two positions ortho to the strongly electronegative groups (structures 3 and 4) would be destabilised relative to the radical position para to the substituent (structure 2). Using the same reasoning we would expect the radical centre ortho to both the electronegative groups(structure 3) to be less stable than when the radical centre is para to the oxygen(structure 4). It could further be argued that the result for the fluoro and methoxy substituents reflects the relative degree of importance of the ionic canonical forms. σ^{0}_{R} values [14] for F (-0.34) , Cl (-0.23) and OMe (-0.45) suggests that the importance of these ionic forms to be in the order Cl<F<OMe. This trend fits our experimental observations in that the substituent group with the greatest mesomeric effect (methoxy) shows the greatest deviation from the general pattern .

However it must be borne in mind that when displacing a hydrogen with a substituent group there must be some degree of steric influence. A comparison between compounds 6 and 7 shows this influence of the steric effect by comparing the amount of the sterically hindered 2-nitro product and the least hindered 6 position. For the case of the relatively small fluoro group there is good agreement between predicted amount of the hindered product and that experimentally determined. For the considerably larger methoxy group however there is a discrepancy which may be accounted for on steric grounds. The amount of the hindered product has been reduced in accordance with the bulkier nature of the methoxy group. The bulkiness of the methoxy group thus appears to accentuate the mesomeric effect by further increasing the amount of the 6-nitro product at the expense of both other nitro products.

Compounds 9-12 contain those groups which are electron withdrawing(-I,-M). The unpaired spin densities predict that there will be little variation in isomer ratio from that of phenol. Our results agree with this prediction except in the case of the 3-nitro compound. In this case the computation did not predict a reduction of spin at the 2 position, in spite of the fact that the nitro group is one of the most powerful electron withdrawing groups. In this case it is not possible to say whether this is a failure in the program adequately to account for the strong electronic perturbations of the nitro group, or some feature of its geometry which results in steric factors unaccounted for by the program.

In the case of compounds 5-8 it is possible that ionic canonical structures contribute to the overall structure of the phenoxy radical. For compounds 9-12 we believe that mesomeric electron withdrawal would tend to destabilize the radical centre and is of less importance. With the exception of the nitro group (compound 12), our observations suggest that the substituents 9-11 have a minimal effect on the product distribution, either by electronic perturbations or steric effect.

Summary

In conclusion, we believe that for phenols the gas-phase IP is a good indicator of the likely success of the two-phase nitration procedure. The upper limit for successful nitration appears to be an IP$<$ 10.0 though reaction is slow at this value and may be of limited synthetic use. There appears also to be a lower limit for the reaction particularly for compounds with a IP $<$ 9.0 and a lower than expected $E_{1/2}$ value as determined by our plot. These compounds are prone to oxidation reactions.

Finally we have shown by their lability and different product ratios that phenols react by a mechanism different to their corresponding phenolic ethers. The nitration mechanism for the ethers appears be either a recombination involving a radical pair (consisting of the radical cation of the aromatic and NO_2) or a nitrosation-oxidation procedure. We believe that all our observations for the phenols tested are consistent with a nitration mechanism involving a phenoxy radical as an intermediate. When no phenoxy proton is present as in the case of the phenolic ethers the rate of the reaction is considerably slower and the product ratio is different, observations consistent with a different mechanism.

In general for the 12 compounds tested there is a reasonably good agreement between predicted and experimentally determined isomer ratios. The product distribution appears to be under the control of two main factors. Firstly the inductive and mesomeric electronic perturbations of the the substituent group on the distribution of the radical . Secondly the physical nature of the substituent group . Final product distribution then reflects an interplay between each of the contributing factors. It would appear that those groups with the greatest influence are those which are electron withdrawing inductively but electron donating mesomerically. In this instance there is some deviation from the expected pattern. This effect is further enhanced when sterically hindered groups are involved and since the MO program does not take this into account, not unexpectedly, the predicted results deviate from the experimental results.

EXPERIMENTAL

Materials

All phenols listed in table 1 were available commercially and used as received, or were prepared by standard literature procedures. Purity was assessed before use by GLC. Solvents were analytical grade and were used without further purification.

Nitration Procedure:

The two-phase nitration procedure was essentially that as described in our earlier report[1] The method is a modification of that described by Kagan [12].

As the nitration of 3-cyanophenol has not previously been reported we describe here its nitration using the two-phase procedure as a typical example, with the exception of the use of dichloromethane as organic solvent in place of diethyl ether.

3-cyanophenol (1.19g, 0.01mol) in dichloromethane (20ml) was added to a stirred mixture of $NaNO_3$ (0.94g, 0.011mol) in 3M H_2SO_4 (10ml). Two crystals of $NaNO_2$ were added and the reaction stirred for 48 hours.The organic phase was separated and the aqueous phase extracted with dichloromethane(2x15ml). The organic phases were combined, washed with water, dried over anhydrous $MgSO_4$ and the solvent removed to yield 1.3g of yellow solid. The total product was chromatographed on silica gel and eluted using 10% ethylacetate:hexane.Three main products were eluted in the following order.

3-Hydroxy-4-nitrobenzonitrile (0.40g), bright yellow solid, mp=105C (lit[13] 102-105), m/z=164.0221 ^{1}H-NMR(d6-Acetone), δ10.2(bs,OH), δ8.1(d, 1H, H-5, J=9 Hz), δ7.5(d,1H, H-2, J=2Hz), δ7.3(dd, 1H, H-6, 9Hz, 2Hz)

3-Hydroxy-2-nitrobenzonitrile (0.35g), pale yellow solid, mp=120-121C (lit[13] 121), m/z=164.0216, ^{1}H-NMR(d6-Acetone), δ10.4(bs,OH), δ7.6(t, 1H, H-5, J=5Hz), δ7.3-7.4(m, 2H, H-4,6)

5-Hydroxy-2-nitrobenzonitrile (0.50g), tan solid, mp=185-187C (lit[13] 185-187), m/z=164.0216 ^{1}H-NMR(d6-Acetone), δ10.4(bs, OH), δ8.10(d, 1H, H-3, J=10Hz), δ7.3-7.2(m, 2H, H-4,6)

Gas Chromatography:

Identification and quantitative analysis of products was achieved by comparison with purified reference samples prepared by standard procedures or with our purified samples. Four different columns were used,

8% OV-17 on Chromosorb W 100 / 120
3% QF-1 on Chromosorb Q 100 / 120
5% SE-30 on Chromosorb W 100 / 120
30m capillary column, liquid phase BP-1

A Perkin-Elmer 8410 gas chromatograph with FID and electronic integrator was used
The total nitration mixture was analysed as the crude product or as the methyl ether after methylation with diazomethane. Corrections were made for flame response where applicable.

Spectroscopy:

Routine ^{1}H-NMR were recorded in $CDCl_3$ solution with TMS as internal standard on a Varian EM-360 (60 MHz) spectrometer. ^{13}C-NMR were recorded in the pulse F/T mode on a JEOL-FX 90Q spectrometer. Signals were recorded in ppm downfield from TMS.

Product Separation

All products from the nitration of compounds in table 1 were isolated by chromatographic procedures. Both gravitational and centrifugal methods used silica gel $60F_{254}$ (Merck) with ethyl acetate:hexane as eluent. Column products were checked for purity by GLC and if required repurified by further chromatography or other methods where applicable. Structures were confirmed by ^{1}H-NMR or by comparison with literature physical data where available.

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