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A THEORETICAL STUDY ON THE TWO-PHASE NITRATION OF PHENOLS

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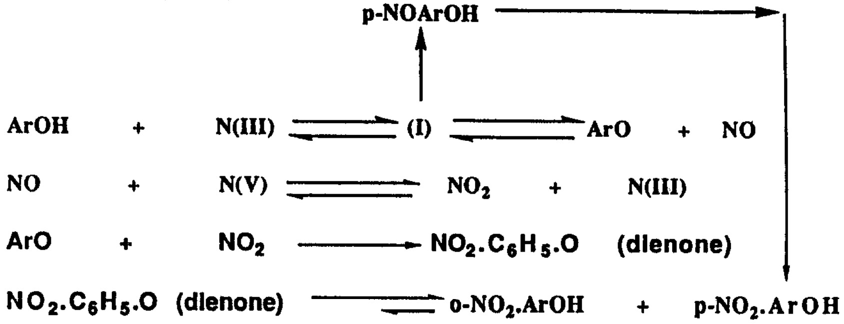
Abstract : The two-phase nitration of phenols is an example of nitrous acid catalysed nitration. Semi-empirical molecular orbital calculations were undertaken on the ground state, radical cation and the phenoxy radical. Unpaired electron spin density calculations can successfully predict isomer ratios for 3-substituted phenols. Catalysis by NO^+ suggests a radical recombination mechanism based on initial electron transfer to form the radical cation followed by proton loss to generate the phenoxy radical.

Introduction

In 1945 Kenner [1] first postulated that a single electron-transfer (E.T.) process may be implicated in electrophilic aromatic nitration. Nagakura[2] showed there to be a strong driving force toward E.T. when the electron affinity of the electrophile is greater than the ionization potential of the aromatic. Pederson, Peterson, Torsell and Lawesson[3] showed a direct correlation between nitration rate and the ionization potential of the aromatic. The authors also showed that substitution occurred preferentially at the sites of the radical cation with the greatest possibility of new bond formation. The concept of E.T. in nitration was rekindled in 1977 by Perrin [4]. He proposed an initial E.T. between the aromatic and the nitronium ion to explain the paradoxical loss of intermolecular selectivity but not intramolecular selectivity for substrates more reactive than toluene.Considerable work has since been done on the involvement of E.T. in nitration , with several excellent reviews[5,6,7,8]. We present here further evidence, this time in the two-phase nitration system, using a series of simple phenols. In our earlier work [9] we re-examined the two-phase procedure (NO_3^- in aqueous acid and organic solvent stirred at room temperature) first described by Kagan[10] and later by Gaude[11] and resolved some of the inconsistencies of the earlier works. We found that on nitration by the two-phase system, m-cresol gave four main products in contrast to Kagan's findings. Our results for nitration of phenol in the presence of nitrite catalysis gave a 1/2 o:p ratio of 0.67. This is in close agreement with the findings of Al-Obaidi and Moodie[13] for the nitrous acid catalysed nitration of phenol in aqueous H_2SO_4. These authors, who concluded that the nitrous acid catalysed nitration is not just a nitrosation -oxidation procedure, suggested the pre-equilibrium formation of an intermediate between phenol and nitrosonium ion. This in turn can form p-nitrosophenol or give rise to the phenoxy radical. The NO generated is then oxidized by the N(V) species in an autocatalytic process.We propose that the two-phase system proceeds by a similar mechanism to that proposed by these authors, the key step being the initial ET to give the intermediate species (I), the exact nature of which is not known.

Proposed nitration mechanism



Results:

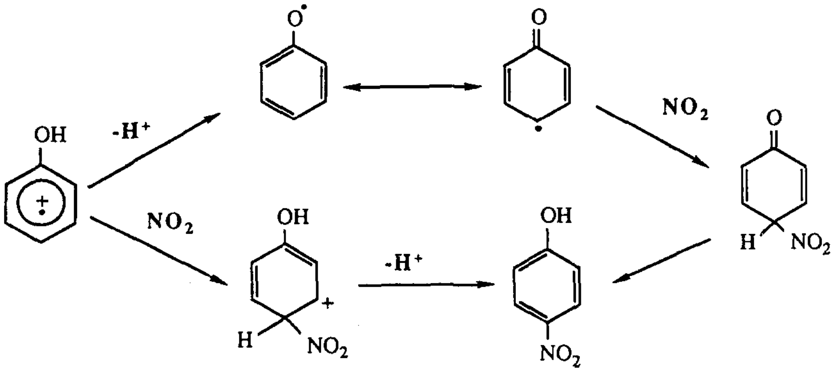
Semi-empirical Molecular Orbital calculations were performed using the Q.C.P.E. Program 506[12] The AM1 SCF procedure was used to determine thermodynamic data, optimised geometries and charge densities for the ground state of the neutral species. Unrestricted Hartree-Foch (UHF) procedure was used for the radical species to determine unpaired electron spin densities. Heats of formation were calculated for the neutral ground state and the radical cation for each of the phenols under study. The results are summarized in Table 1. In each instance the formation of the radical species was highly endothermic. Reference data was used for the thermodynamic values for NO and NO_2. Using the procedure of Feng, Zheng and Zerner[14] we determined the energy for ET for the formation of the radical cation using NO^+ as the transfer agent as follows:

$$ArOH + NO^+ \longrightarrow ArOH^{+\bullet} + NO$$

Table 2 shows that the calculated energy of this electron transfer, ΔE_{ET}, is favourable for all compounds listed and of similar value. It must be borne in mind however that these figures refer to gas phase energetics and the nature of the solvent has not been taken into account. We have used 12 different organic solvents with dielectric constant ranging from D = 2 (n-hexane) to D = 35 (acetonitrile) in the two-phase procedure. Nitration proceeded effectively and rapidly in each of the solvents, but for ease of work-up , minimization of tarry products and maximization of nitrated products, diethylether was the solvent of choice.The nature of the solvent would be expected to have a bearing on the ease of the ET, as the ionic species such as the NO^+ would be preferentially stabilized in media of high dielectric constant. Our experimental results suggest that the nature of the solvent and ΔE_{sol} have a minimal effect on the ET at least for phenols under our reaction conditions.

We suggest NO^+ as the electron transfer agent in preference to NO_2^+ as Eberson and Radner [15] in their excellent review of 1987 showed the former to be a far superior ET agent. The authors based their argument on Marcus theory calculations which showed there to be a considerable difference in the reorganizational energy between NO^+ and NO_2^+ in going to the neutral compound. Further the authors showed that in solution radical cations are readily formed in high concentration by ET to NO^+, by all the compounds tested which had an E^o < 1.8V. Also to be taken into account is that NO^+ is a much weaker electrophile than NO_2^+

Considerable evidence has been presented recently for the role of E.T. involvement in the nitrous acid catalysed nitrations of N,N-dimethyl aniline[16], p-nitro phenol[17], phenol[18] and mesitylene[19]. On the basis of kinetic data and CIDNP experiments respectively, Al-Obaidi and Moodie[13] and Ali, Ridd, Sandall and Trevellick[2] suggested the intermediacy of a phenoxy radical in the nitrous acid catalysed nitrations. Ridd et al showed that the nuclear polarization was not due to the radical pair from the initial electron transfer but from a phenoxy radical formed in a reversible process.
By ^1H and ^{13}C-NMR we have observed the ipso nitro intermediate, believed to be 4-methyl-4-nitrocyclohexa-2,5-dieneone, from the nitration of p-cresol using NO_2 / $CDCl_3$ at -20°C. In the ^1H-NMR we observed two doublets for the vinylic protons (δ7.10(d), J = 10 Hz. and δ6.38(d), J =10 Hz.) and a sharp singlet (δ1.95) for the methyl group. The signal at δ7.10 does not agree with the findings of Clemens et al[21a] who found a signal more upfield at δ5.66. Allowing the nitration mixture to warm to room temperature resulted in the rapid collapse of these signals as the intermediate was converted into 2-nitro-4-methylphenol. Similar signals for ipso-nitro intermediates were observed when 4-ethyl and 4-t-butylphenol were nitrated under similar conditions. We did not observe the ^{13}C-nuclear polarization from the aromatic components as reported by Ridd et al[21].
In an attempt to show the possible role of the phenoxy radical in the nitration mechanism the heats of formation of the phenoxy radical by proton loss from the corresponding radical cation have been calculated. Table 2 summarizes these results. There is a large negative heat of formation for each of the phenoxy radicals with no corresponding value for the anisole. It seems possible then that the loss of a proton from the radical cation may be more rapid or more favourable than the formation of a Wheland intermediate with NO_2. We thus suggest the possibility of two opposing mechanisms for further reaction of the radical cation , each leading to the possibility of nitrated products. Based on product isomer ratios we favour the phenoxy radical sequence.



In his excellent review on the reactions of phenols, Ershov[26], discussed the intermediacy of dienones in electrophilic reactions. The author showed that phenoxy radicals, depending on the structure of the original phenol, can subsequently react in two different forms, corresponding to the ortho and para quinolide forms. Generally phenoxy radicals with an unpaired electron on the oxygen atom have a short half life and tend to isomerize. However, in the presence of other radicals(particularly when in excess), dimerization may be supressed, and the phenoxy radical stabilized by recombination with the other radical.

Table 1

Calculated Ionization Potentials (eV) and Heats of Formation (k cal mol.$^{-1}$) by AM1

	IP(calc)	IP(ref)	ΔH_f (GS)	ΔH_f (Ion)	$\Delta(\Delta H)$
Phenol	9.11	8.51	-22.24	173.10	195.34
2-Methyl	8.99	8.51	-29.41	162.49	191.19
3-Methyl	9.02	8.52	-29.80	162.97	192.77
4-Methyl	8.88		-29.79	160.32	190.11
3-Ethyl	9.01		-35.07	156.61	191.68
4-Ethyl	8.92		-35.56	154.67	190.23
3-t-Butyl	8.98		-35.07	149.86	188.84
4-t-Butyl	8.89		-40.58	148.31	188.89
Anisole	8.90	8.22	-15.85	174.84	190.69
3-Me-anisole		8.31			
NO(ref 33)		9.25	21.50	235.00	213.50
NO_2(ref 33)		9.79	7.89	233.00	225.11

Table 2

Calculated Energies for Electron-Transfer for the formation of the Radical cation using NO^+ as the transfer agent, and ΔH for the subsequent loss of a proton to give the Phenoxy radical.

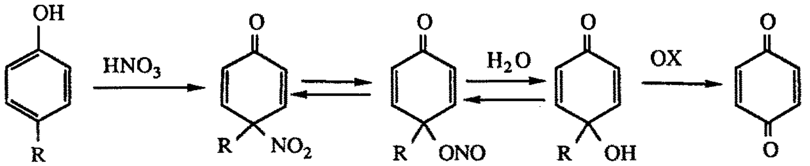
1) $ArOH + NO^{+} \longrightarrow ArOH^{+\bullet} + NO$

2) $ArOH^{+\bullet} \longrightarrow ArO^{\bullet} + H^{+}$

	E_{ET}, k.cal.mol^{-1}	ΔH, k.cal.mol^{-1}
Phenol	-18.16	-177.82
2-Methyl	-22.31	-166.04
3-Methyl	-20.73	-165.49
4-Methyl	-23.39	-164.27
3-Ethyl	-21.82	-173.01
4-Ethyl	-23.27	-164.23
3-t-Butyl	-24.66	-163.95
4-t-Butyl	-24.61	-162.92
Anisole	-22.80	---------

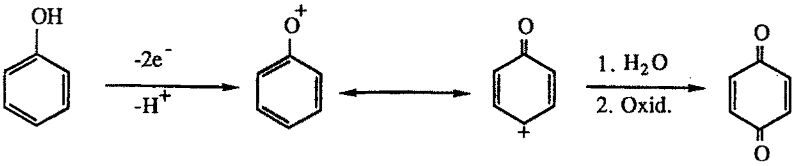
Calculated unpaired electron spin densities of a series of phenoxy radicals are shown in Table 3. In each case the highest spin density is located at the C-4 carbon , followed by the C-6 and C-2 carbons. The relative spin densities of the ring positions were used to determine the amount of substitution at each position. These results are shown in Table 4. For phenol, 3-methylphenol and 3-ethylphenol, there is a very good correlation between the predicted and found isomer ratios. For 3-t-butylphenol we expect that the bulkiness of the t-butyl group hinders substitution at the 4 and 2 positions thus favouring the 6 position. Product isomer ratios show this to be the case. For the 4-substituted phenols the radical spin density would predict initial substitution at the ipso carbon, a result in agreement with those of Feng, Zheng and Zerner[14] and also observed by Ali, Ridd, Sandall and Trevellick[21].

For phenol and the 2 and 3-substituted phenols a significant product was a quinone (2-8%). Quinones have previously been described as oxidation products in the reaction of phenols[23,24]. Our data suggest that formation of these quinones is a competing reaction with nitration at the 4 position. When the amount of quinone product is added to the 4-nitro product , the total product ratio agrees very well with the predicted products except for the t-butylphenol as previously stated. Ershov[26] suggested that the quinones are a result of the intermediacy of quinonitrols, which if formed readily decompose to give quinols. The quinol in turn can be oxidized to the quinone depending on the nature of the R group. Recently Ridd[25] has shown the reversible nitro-nitrito rearrangement following the ipso attack in the nitration of p-cresol can give a quinol.



In a separate series of experiments we prepared several hydroquinones using standard literature procedures[27,28] and together with the parent hydroquinone (1,4-dihydroxybenzene) subjected each to the two-phase nitration procedure. After an overnight reaction time they were in each instance largely converted to the corresponding quinone with no nitrated products evident.

An alternative method by which the quinone can be formed is by a second ET involving the phenoxy radical and NO^+ to form a phenoxonium cation .This in turn can undergo a nucleophilic attack by water to form the hydroquinone. Oxidation then gives the quinone.

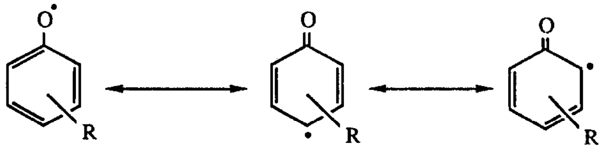


Vermillion[32] suggested a 2-electron oxidation to explain the observed 10% product formation of a benzoquinone in the electrochemical oxidation of 2,6-di-t-butyl-4-methylphenol in buffered aqueous isopropanol. Reaction was thought to proceed via a phenoxonium ion.The author further suggests the decarboxylation of an intermediate acid in an overall ten electron process. The relatively high yield of a methoxycyclohexadienone is cited as evidence to confirm the phenoxonium ion mechanism.

Table 3

PHENOXY RADICALS

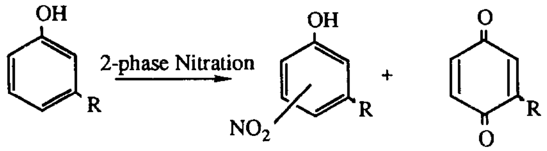
Unpaired electron spin density of phenoxy radicals using AM1 SCF (UHF) method



	C-1	C-2	C-3	C-4	C-5	C-6	O
R = H	0.0322	0.2199	0.0043	0.3847	0.0042	0.2208	0.1338
R = 2 Me	0.0343	0.3029	0.0001	0.3294	0.0108	0.1397	0.1239
R = 3 Me	0.0314	0.1972	0.0049	0.3950	0.0038	0.2387	0.1310
R = 4 Me	0.0303	0.1908	0.0082	0.3987	0.0079	0.1840	0.1117
R = 3 Eth	0.0302	0.1978	0.0049	0.3936	0.0042	0.2336	0.1311
R = 4 Eth	0.0307	0.1928	0.0074	0.3975	0.0074	0.0192	0.1152
R = 3-tBu	0.0322	0.1987	0.0043	0.3950	0.0048	0.2304	0.1306
R = 4-tBu	0.0309	0.1979	0.0081	0.3984	0.0073	0.1853	0.1150

Table 4

Product isomer ratios of 3-Substituted Phenols



R	Product	% Predicted based on unpaired Spin density of the Phenoxy Radical	% Found by G.L.C.
H	**2 NO_2**	**53.2**	**55.1**
	4 NO_2	**46.6**	**41.3**
	Quinone	**----**	**2.1**
Methyl	**2 NO_2**	**23.3**	**22.5**
	6 NO_2	**28.9**	**27.9**
	4 NO_2	**47.8**	**41.0**
	Quinone	**----**	**7.3**
Ethyl	**2 NO_2**	**23.9**	**20.5**
	6 NO_2	**28.3**	**29.9**
	4 NO_2	**47.7**	**41.4**
	Quinone	**---**	**5.6**
t-Butyl	**2 NO_2**	**24.1**	**19.3**
	6 NO_2	**28.0**	**40.7**
	4 NO_2	**47.9**	**34.8**
	Quinone	**----**	**2.9**

One further line of evidence for the phenoxy radical mechanism is the reactivity of anisole toward the two-phase nitration procedure. Anisoles in general would be expected to behave similarly to the corresponding phenols[5] toward nitration procedures. Our gas phase thermodynamic data would support this argument. However, when anisole and its 3-methyl analogue were subjected to the two-phase nitration procedure no nitration products were detected. Catalysis with added nitrite and prolonged reaction time had little effect. We suggest two possibilities to explain this observation:

1) anisoles have no hydroxy proton , thus cannot readily form the phenoxy radical from the radical cation if this is formed. This could further suggest that NO_2 does not add to the radical cation.
2) the anisoles tested cannot be oxidized by an ET to NO^+ under the reaction conditions employed in the two-phase procedure.This suggests that solution energetics are not directly comparable to gas phase energetics.

Based on reference[33] gas phase ionization potentials for phenol (8.51eV), anisole (8.22eV) 3-methyanisole (8.31eV) and NO (9.25eV) , ET between each of these aromatics and NO^+ would be expected to energetically favourable. Zerner et al [14] suggested that a radical-pair recombination mechanism would be favoured whenever the ionization potential of the aromatic is much less than that of NO_2. Eberson[7] suggested that the upper limit for the formation of the radical cation in solution was a potential of E^o=1.88V for the organic compound with NO^+ as the oxidant. Miller[31] measured the half-wave potentials of a series of organic compounds in acetonitrile and found that phenol has an abnormally low value of $E_{1/2}$=1.04V (E^o=1.60V). Anisole was found to have an $E_{1/2}$=1.40V (E^o=1.98V). This difference was largely attributed to the variable solvation effects between the phenol and the anisole and their respective radical cations. Using E^o=1.51V for NO^+ and $\Delta G^o = -23.06\ (E^o_{NO} - E^o_{Ar})$ makes ET between anisole and NO^+ endergonic at 10.8 k.cal.mol^{-1}. This may be too energetically unfavourable for reaction to occur. Similarly for phenol ET is endergonic but with a much lower ΔG^o= 2.3 k.cal.mol^{-1}.

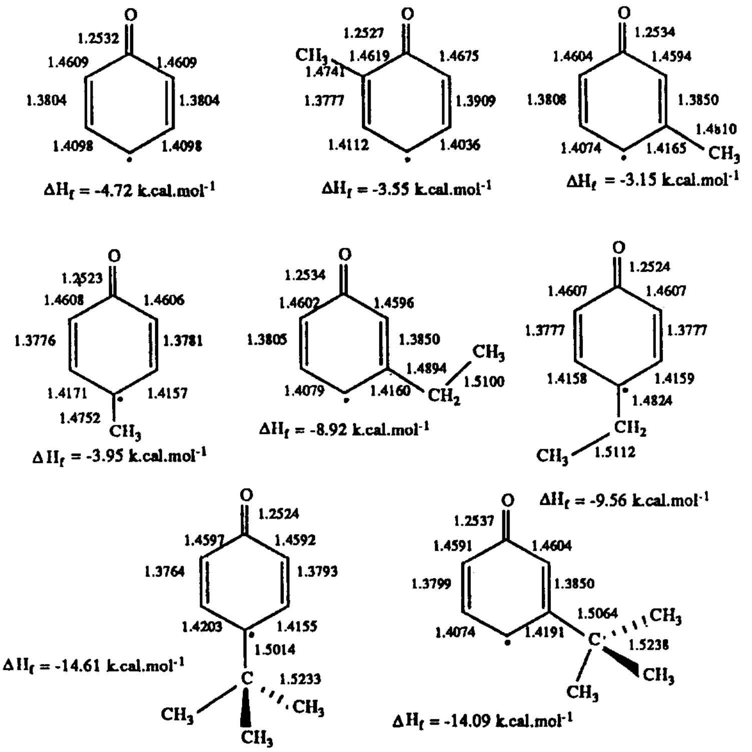
Eberson proposed that ET may be feasible inspite of an unfavourable energy change (up to a value of 23 kcal.mol^{-1}) when subsequent events are exergonic and thus provide the driving force for the reaction sequence.The energetically favourable loss of a proton (by our calculations) from the phenol radical cation we propose as being an example. No such driving force is available to the anisole radical cation.

As was the case for the phenols, a range of organic solvents was used in the two-phase procedure for the anisoles . No nitrated products were observed in any of the solvents tested suggesting that the nature of the solvent has no effect.

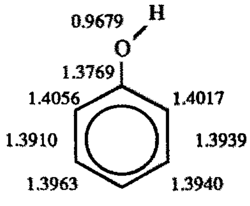
Calculated optimised geometries

All geometries and thermodynamic data were calculated without any assumptions and all variables were free to optimize using the AM1 SCF method.The structures were proven to be energy minima by Force calculations. Our structures are similar to those of Feng, Zheng and Zerner[14] using MNDO and Politzer et al[29] and Gleghorn[30] using ab-initio methods for benzene and nitrobenzene derivatives. Of particular interest is the geometry of the NO_2 group in the nitro phenol products. In o-nitro and p-nitrophenol as expected the NO_2 is co-planar with the ring. The same applies to the 4-nitro and 6-nitro isomers of m-cresol. In the hindered 2-position, however, the NO_2 group is twisted out of plane by 12 degrees. In the considerably more hindered 2-position of 3-t-butylphenol the NO_2 group is now twisted out of plane by 51 degrees and the hydroxy proton is now also well out of plane. In the 4-position, without the influence of the hydroxy group, the NO_2 group is out of plane by 64 degrees. The changing nature of the orbital interaction between the NO_2 group and the aromatic ring is reflected in the physical properties of the 3-t-butylphenols, 6-nitro-3-t-butylphenol is a yellow oil, 4-nitro-t-butylphenol is a low melting solid and 2-nitro-t-butylphenol is a colourless solid with m.p. of 100 C. Similarly in the ^{1}H-NMR a more upfield shift was observed for the proton ortho to the NO_2 group as the degree of non planarity increased, suggesting a reduced mesomeric electron withdrawing effect.

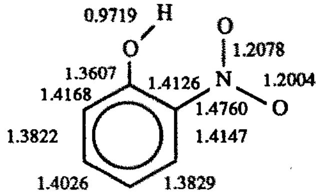
Optimized structures of the phenoxy radicals by AM1 SCF (UHF), bond lengths in angstroms



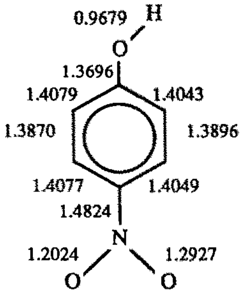
Optimized structures for phenol and its nitro derivatives, bond lengths in angstroms



ΔH_f = -22.24 k.cal. mol$^{-1.}$

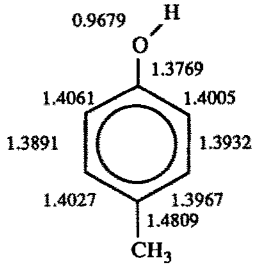


ΔH_f = -20.17 k.cal .mol.$^{-1}$

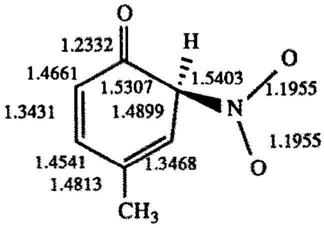


ΔH_f = -19.56 k.cal. mol.$^{-1}$

Optimized structures for p-cresol and its nitro derivatives, bond lengths in angstroms



ΔH_f = -29.79 k.cal.mol^{-1}



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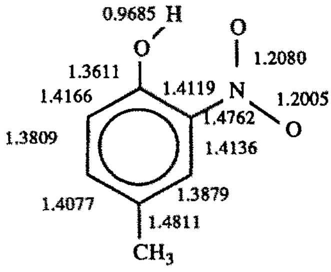

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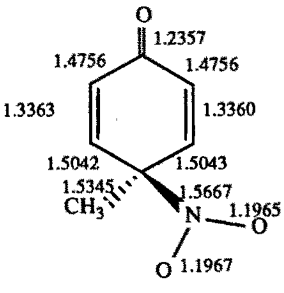

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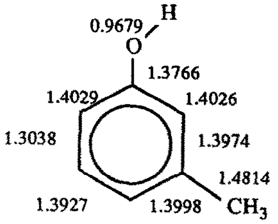
Optimized structures of 3-methylphenol and its nitro derivatives, bond length in angstroms.



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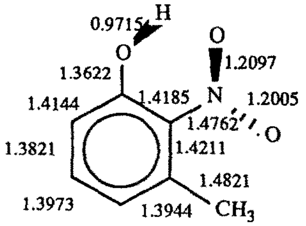

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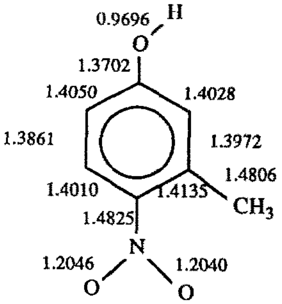

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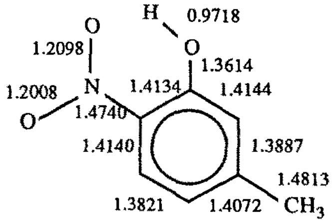
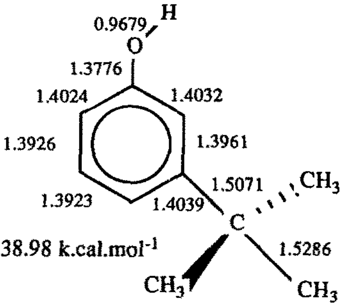


ΔH_f = -28.17 k.cal.mol^{-1}

Optimized structures for the 3-t-butylphenol and its nitro derivatives,bond lengths in angstroms



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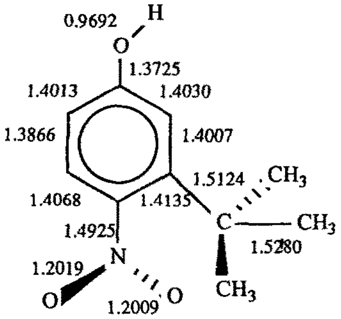

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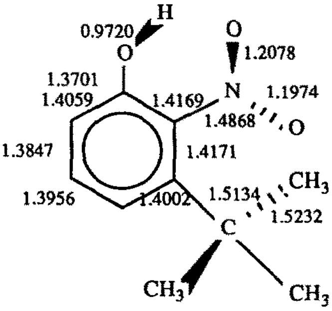

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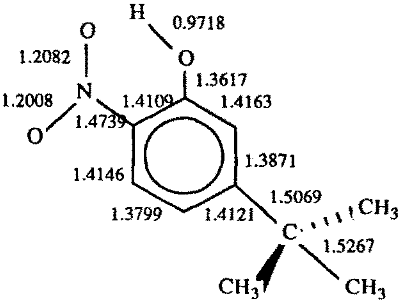

ΔH_f = -39.17 k.cal.mol^{-1}

Conclusions

We conclude that the nitration by the two-phase procedure may involve more than one mechanism. The isomer ratios suggest it is not a nitration by NO_2^+, nor solely nitrosation followed by oxidation. Our observations suggest a nitrous acid catalysed mechanism involving initial ET to NO^+ and the intermediacy of the phenoxy radical. Radical recombination between the phenoxy radical and NO_2 determines the product ratio. Increased H^+ concentration and catalysis by added NO_2^- speeds up the reaction without affecting product ratios. Conversely addition of a nitrous acid trap, such as urea, suppresses nitration. Nitration of phenol and m-cresol using a modification of the NO_2 / CH_2Cl_2 procedure of Eberson and Radner [15] gave product isomer ratios almost identical to those obtained by the two-phase procedure. We suggest these two procedures each involve initial ET to the NO^+ generated by the oxidation of the aromatic and may be one and the same. Similar amounts of benzoquinone, an oxidative by-product were found in both procedures. The anisoles tested failed to nitrate by the two-phase procedure, a result in agreement with the observed behaviour in nitrous acid catalysed nitrations in aqueous acid. Gas-phase ionization potentials predict that the nitration by a radical-pair recombination would be successful. Solvent dependent oxidation potentials show this not to be the case, though the nature of the solvent would appear to have a minimal effect. Finally we have also demonstrated by MO calculation good correlation between unpaired electron spin density of the phenoxy radical and product isomer ratio when ipso nitration is not a complicating factor. No such good agreement was found when using the charge density of the phenol or the spin density of the radical cation to predict the isomer products. Spin density values can also be used to predict ipso nitration leading to nitro-dieneone intermediates which we have observed at low temperature.

EXPERIMENTAL

Nitration Procedure:

The two-phase nitration procedure was essentially that as described by Kagan[9]. We used H_2SO_4 in preference to HCl and catalysis by added $NaNO_2$. After completion of the reaction the ether phase was removed and the nitro isomers separated by chromatography. Both gravitational and centrifugal methods used silica gel $60F_{254}$ (Merck) with ethyl acetate : hexane as eluent.

Gas Chromatography:

Identification and quantitative analysis of products was achieved by comparison with purified reference samples prepared by standard procedures. Three 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

A Perkin-Elmer 8410 gas chromatograph with FID and electronic integrator was used.

Spectroscopy:

Routine ^1H-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.

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