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AUTOXIDATION OF *p*-HYDROXYDIPHENYLAMINE

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Abstract—Autoxidation of *p*-hydroxydiphenylamine (HDPA) gives N-phenyl-*p*-benzoquinoneimine and hydrogen peroxide as primary products over a wide range of pH and the previously reported formation of N-(4-hydroxyphenyl)-*p*-benzoquinoneimine in basic media is in error. An induction period which is independent of substrate concentration but decreases with increase in pH is observed. The rate of oxidation is first order with respect to oxygen and half order with respect to HDPA. Oxygen is used in the system at the rate comparable to its rate of dissolution. On the basis of various kinetic parameters, a mechanism involving electron transfer to oxygen from HDPA anion and subsequent formation of HO_2 radical is postulated. The agreement of the experimental results with the derived rate expression is shown to support the mechanism.

Singlet oxygen, produced *in situ* by methylene blue sensitization, leads to oxidation but with different products indicating that this species is not involved in the autoxidation.

Mechanisms of autoxidation of organic substances are of considerable importance so as to exercise a control over these processes in order to enhance or prevent them, as required. A perusal of literature shows that these reactions are quite complex;[1] primary products are often transformed by secondary reactions[2,3] and radicals are the common chain propagators.[4,5] In some autoxidations, $O_2(^1\Delta_g)$[6,7] or carbanions[8,9] are also known to be involved.

Phenols and anilines are the most often used antioxidants which terminate oxidation chains through H-atom transfer;

$$RO_2^{\cdot} + HOR(\text{or } HNR_2) \longrightarrow RO_2H + RO^{\cdot}(\text{or } R_2N^{\cdot}).$$

An ESR study of the inhibitory effect of diphenylamine has shown the presence of a stable radical, diphenylnitroxide, which is possibly formed from diphenylnitrogen and peroxy radicals.[10] Hydroxylamine is known to undergo autoxidation in a pH dependent reaction where a deprotonated hydroxylamine species and oxygen are involved in the rate determining step.[11]

p-Hydroxydiphenylamine on prolonged standing gives a dark brown solid and we were interested in understanding this oxidation change. From an autoxidation point of view there are two active centres present in this molecule and it was felt that we might be able to evaluate the relative activity of these centres towards oxidation from the extent of reaction and product analysis. Another objective of the investigation was to examine the role of singlet oxygen in the oxidation by generating this reactive species *in situ* by the well known dye photosensitized process.[12-14]

EXPERIMENTAL

p-Hydroxydiphenylamine (HDPA) (K & K Laboratories) was first distilled with superheated steam (180°) and then crystalized from benzene/hexane mixture. The UV spectrum of this purified amine quantitatively agreed with the reported spectrum.[15] Acetonitrile was BDH grade and was distilled before use. Allyl alcohol (Merck's Germany) was used as such. Other solvents were of AR grade and were distilled before use. For stock solns of HDPA the solns were prepared in deaerated solvents. The deaerations were done with hydrogen (99.9%).

For actual runs a special reaction cell (10 cm × diam 1.6 cm) with a side capillary tube was used. The cell could be directly transferred to the spectrophotometer. For oxygenation, presaturated O_2 was passed through the solution. The yellow coloured product was extracted with ether and the ether layer was washed repeatedly with distilled water. Since the initial product further reacted the conversions were kept low and the experiment was repeated 5–6 times to collect enough product for analysis. The combined ether extract was chromatographed on a TLC silica gel "G" plate (benzene as developer) and analyzed.

The reaction was found to be very fast in water and mixtures of water and acetonitrile were used to control the rate. All the experiments were done at 32 ± 1°. After establishing the identity of the products the reaction was monitored at 4480 A in the kinetic runs. It was ensured through a final spectrum of the reaction product mixture that the same product was formed in all the experiments.

In dye sensitization, methylene blue (λ_{max} 6450 A) was used as a sensitizer. The photolysis cell consisted of a pyrex tube (170 mm × dia. 24 mm) over which a small water condenser was fitted. The gas tube was adjusted so that it was not in the light path. A high pressure mercury lamp (125 W, Philips India) fed from a stabilized power supply with a filter having a cut off at 4700 A was used for irradiations. The products analyses were done in the same manner as described above.

RESULTS AND DISCUSSION

Product analysis. At low conversions (below 4%) two products were formed. N-(phenyl)-*p*-benzoquinoneimine (PBQ) was identified by its m.p. 101-2° (lit.[16] – 101.5°), UV spectrum (λ_{max} – 2640 A, 4480 A) and by comparison of NMR spectrum with the authentic sample.[17] H_2O_2 was identified and measured by its complexing with titanium sulphate.[18] A plot of product concentration vs reaction time for each of PBQ and H_2O_2 was linear showing that both are primary products.

Effect of O_2 *concentration and flow rate.* In kinetic runs the conversions were kept below 1.5%. For varying the concentration of O_2, mixtures of O_2 and H_2 of various proportions but constant total pressure were passed through the soln at constant flow rate of 36 ml min^{-1}. The results are shown in Table 1. The reaction rate is proportional to O_2 concentration and first order with respect to it.

The rate was dependent on flow rate and increased to a constant value at flow rate of 35 ml min^{-1}. This shows that O_2 is rapidly depleted during the reaction and the depletion rate is comparable to dissolution rate of O_2 in the solvent.

Effect of substrate concentration. The concentration of

Table 1. Effect of O_2 concentration: [HDPA] = 5×10^{-3} M; acetonitrile : water (1 : 1); temperature = 32 ± 1°C

O_2 pressure (mm of Hg)	$[O_2] \times 10^4$ (ml^{-1})	Relative reaction rate $\times 10^6$ (ml^{-1} min^{-1})	$\frac{\text{Rate}}{[O_2]} \times 10^2$
675.5	11.41	3.371	0.30
307.0	5.184	1.912	0.36
241.2	4.074	1.512	0.37
161.0	2.719	0.938	0.35

HDPA was varied from 2.0×10^{-3} M to 5.0×10^{-3} M. O_2 was passed at a constant rate (Fig. 1 shows the results). The rates are linear and the same product is produced in the initial and final stages as observed from the absorption spectra in the visible region. There is an induction period which appears to be independent of the substrate concentration.

Effect of H^+ *concentration.* The pH of the soln was varied with HCl or NaOH between 4.7 and 10. In view of very low conversions buffering was not necessary (Fig. 2 gives the results). There is a dramatic effect of $[H^+]$ and the induction time was found to decrease with the increase in pH. The decrease in induction time is in accordance with the building up of the concentration of a reaction intermediate during this time since in a faster reaction the concentration is expected to reach its steady state value in a shorter period. It is to be noted that an increase in the autoxidation of anthranol with decrease in $[H^+]$ has previously been observed.[19]

Raevskii *et al.* have reported the product N-(4-hydroxyphenyl)-*p*-benzoquinoneimine in the oxidation of HDPA in the presence of KOH.[20] We have carefully looked at the products at higher pH value and have found the same product PBQ as in neutral solutions. It may be noted that there is a considerable difference in the absorption spectra of N-(4-hydroxyphenyl)-*p*-benzoquinoneimine and PBQ.[21]

Effect of ionic strength. The ionic strength of the reaction was varied by the addition of $NaNO_3$ and the results are given in Table 2. The results are not very conclusive but appear to support the participation of ions in the mechanism.

Effect of addition of radical trap. Allyl alcohol has been successfully used for trapping radicals.[22] We introduced allyl alcohol into the system in varying amounts. Figure 3 gives the results. There is an increasing decrease in the rate with increase in allyl alcohol concentration. There is, however, no significant change in the induction period.

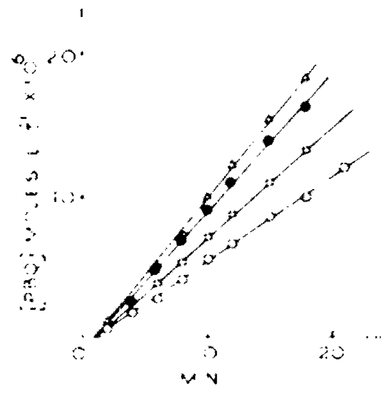


Fig. 1. Effect of HDPA concentration. Solvent = acetonitrile : water (3 : 2); ○, 2×10^{-3} M; □, 3×10^{-3} M; ●, 4×10^{-3} M; △, 5×10^{-3} M. O_2 flow rate 27.3 ml/min.

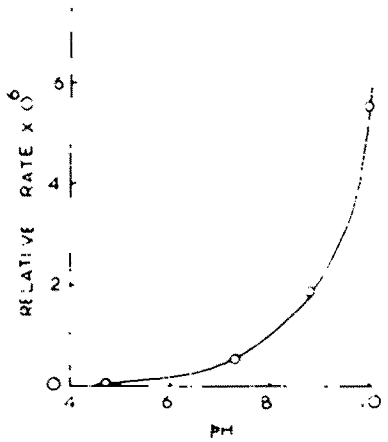


Fig. 2. Effect of pH. HDPA = 5×10^{-3} M; solvent = acetonitrile : water (1 : 1); O_2 flow rate = 35 ml/min.

Table 2. Effect of addition of $NaNO_3$: [HDPA] = 4.0×10^{-3} M; acetonitrile : water (1 : 1); temperature = 32 ± 1°C

$NaNO_3$ (M)	Relative reaction rate $\times 10^6$ (ml^{-1} min^{-1})
0	3.65
0.05	2.83
0.125	2.69
0.25	2.66

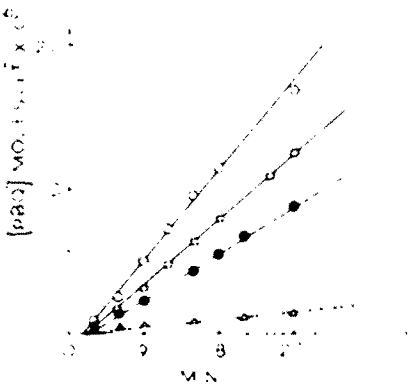


Fig. 3. Effect of allyl alcohol concentration. HDPA = 2.5×10^{-3} M. Solvent = acetonitrile : water (3 : 2); ○, 0 M; □, 2.95×10^{-3} M; ●, 5.89×10^{-3} M; △, 17.6×10^{-3} M; O_2 flow rate = 27.3 ml/min.

Effect of hydrogen peroxide and water concentration. H_2O_2 is a product in the reaction and it was found to enhance the reaction when added to the system. In another set of experiments the concentration of water in acetonitrile medium was varied. Table 3 shows the results. The rate increases with water concentration but in no simple manner. The effect does not appear to be a pure dielectric effect.

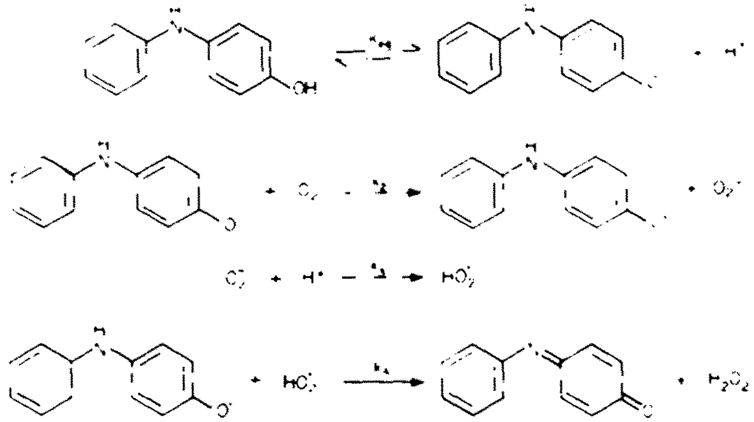
Mechanism. Since there is only one product formed

Table 3. Effect of water concentration: [HDPA] = 1.0×10^{-3} M; temperature = 32 ± 1°C

Water in† acetonitrile	Relative reaction rate × 10' (ml^{-1} min^{-1})
0	0.17
30	1.39
40	3.13
50	9.73
60	34.76
70	66.96
80	130.40

†Values % water

under different [H$^+$] conditions and one would expect bonding of a proton with the lone pair of electrons of nitrogen in the HDPA molecule at lower pH values and greater proton abstraction from OH group at higher pH values, it appears that there is only one reactive centre. A mechanism which is consistent with the various kinetic parameters is:



under the steady state assumption the rate of the reaction is given by

$$\text{Rate} = \frac{d[\text{PBQ}]}{dt} = k_4\sqrt{K_{eq}}[O_2][\text{HDPA}]^{1/2}.$$

This expression predicts first order kinetics with respect to O_2 as observed and half order with respect to HDPA. Figure 4 gives the plot for relative rates vs [HDPA]$^{1/2}$ which is linear and supports the proposed mechanism. The effect of water can be due to the complexation of the proton to give hydronium ion giving a larger concentration of the amine anion or stabilising effect on other intermediates and somewhat polar transition state.

In the dye sensitization solutions of 5×10^{-3} M HDPA and 4.14×10^{-5} M methylene blue were photolysed in acetonitrile containing 2% water in the presence of O_2. Water was used because the quantum yield in pure acetonitrile was very small. The product mixture had a very different absorption spectrum as compared to pure autoxidation. Methylene blue in which the singlet-triplet splitting is known to be small[23] is expected to either transfer energy to O_2 through triplet-triplet annihilation or abstract an electron from HDPA which may be followed by a proton transfer.[24] However these two pathways can

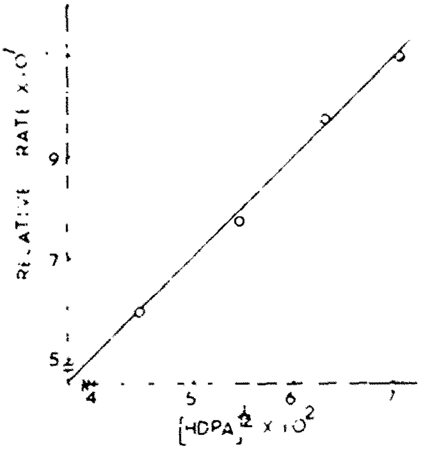


Fig. 4. Plot of relative reaction rates vs square root of HDPA concentration. Solvent = acetonitrile : water (3 : 2); O_2 flow rate = 27.3 ml/min.

be distinguished by using singlet O_2 quenchers.[25] We used *β*-carotene and diazabicyclo (2:2:2) octane[26] as probes. The reaction was found to decrease in both the cases indicating the presence and participation of $O_2(^1\Delta_g)$. It is thus clear that singlet O_2 does bring about the oxidation of HDPA but certainly through a different route as compared to that of autoxidation.

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