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EFFECTS OF UV LIGHT ON DILUTE AQUEOUS SOLUTIONS OF *m*- AND *p*-NITROPHENOL

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Abstract—Circumstantial evidence derived from an exploratory study by different methods suggests that the effect of UV light on dilute aqueous solutions of *m*- and of *p*-nitrophenol is largely nitrite displacement by OH^- nucleophile from the solvent, with formation of HNO_2 in the initial stages. Dilute aqueous picric acid solutions behaved in a manner more or less similar to that of the mononitrophenols and also similar to that of its methanolic sodium methoxide solutions as has been reported in the literature. In all cases, when ultimately the aqueous solutions are decolourized, photofragmentation seems to ensue.

It has been suspected that the unusual difficulty which prevailed for a long time, in obtaining reproducible conductances and concordant pK values for picric acid in aqueous solution by various methods including spectrophotometry,[1] could be due to lack of control of photolytic decomposition. This suspicion was based on Jaeckel's brief study[2] which had not been extended.

We have therefore pursued Jaeckel's study with the addition of certain other investigations, and the inclusion of *m*- and *p*-nitrophenols, as an exploratory contribution towards a quantitative and mechanistic study of the reaction(s) taking place, as would be based on complete product analyses and quantum efficiency determinations.

Our experiments consisted in irradiating aqueous solutions in the 10^{-5} M–10^{-3} M concentration range with un-filtered light from a "Quarzlampon Q81" high pressure source in a specially designed thermostated reactor. The design enabled the photolysis to be conducted in an atmosphere of purified nitrogen. Gaseous products were passed through a scrubbing vessel containing pure water, the pH of which was monitored continuously. The immersed UV source had a relative spectral energy distribution of 100 at 366 nm, 46 at 254 nm and 44 at 405/8 nm. The deliberate omission of filters at this stage was meant to establish some relevance of the photolysis under these conditions to the un-controlled conditions of exposure of solutions in the course of conductance, e.m.f. and other studies. Purified samples of solutes and solvents were used.

The photolysis was followed by (a) pH measurement, (b) conductance measurement, (c) spectrophotometric scanning over the range 185–450 nm, and (d) pH titration against a standard carbonate-free alkali solution of appropriate concentration.

Both the titration and pH data, for various initial HPic concentrations, indicate an initial increase in acidic content followed by a decrease which ultimately leads to a neutral solution; this appears to be the pure solvent. The initial increase may be explained by the formation of a stable acidic intermediate, conceivably nitrous acid (perhaps partially converted to nitric acid) resulting from elimination of one (or more) nitro groups from the aromatic nucleus, and their substitution by OH^- from the solvent. The scission of the C–N bond(s) is consistent with the bond strength being 305 kJ mole^{-1} and the highest relative spectral energy distribution of the lamp used being at 366 nm, which corresponds with a spectral energy in the 300–400 kJ mole^{-1} range. Prolonged photolysis would eventually lead to the decomposition of the nitrous (or nitric) acid by-product, whereafter photofragmentation of the partially "de-nitrated" main product presumably ensues, as seems evident from the UV-visible spectra which reduce to the mere base-line (Fig. 1).

In a few runs, using external source, the brucine test for nitrate[3] (limit of identification 0.66 μg HNO_3) carried out on partially photolysed solutions was positive. The shapes and number of inflexions of the pH titration curves indicated the presence of mixtures of acids, which might include HNO_2/HNO_3 and the remainder of HPic, possibly as well as a much weaker one which might also be dibasic.

An attempt has been made in this study to monitor the formation of HNO_2 or HNO_3 spectrophotometrically, by running the UV-visible spectrum of a mixture of HNO_3 and HPic solutions of concentrations that would sensibly be present in a photolysed HPic solution. The bands of these two components are similar at the shorter wavelengths and no new features could be distinguished in the mixture in that region. At longer wavelengths, HNO_3 has a moderately strong band with its maximum at 301 nm. When this is superimposed on the HPic strong band (max at 356 nm) a mere hump appeared on the latter. This also seems to have had the effect of shifting its min from 284 nm to 278 nm. In the present spectra of photolysed HPic solutions, no hump is noticed, presumably because of the very low concentrations of HNO_3 present, but a systematic blue shift of the minimum at 284 nm is noticeable (Fig. 1). However, since the photolysed solutions are eventually decolourised completely, it is reasonable to assume that this occurs through the loss of the strongly chromophoric nitro groups. Nitro group elimination from one position may be assumed to proceed to completion but in this case the titration data (Fig. 2) would suggest that, since in no case has the increase in acidic content reached even 100%, the HNO_2 (or HNO_3) by-product is perhaps decomposed simultaneously.

Apart from all the curves in Fig. 2 showing an initial increase in acidic content, followed by a decrease to

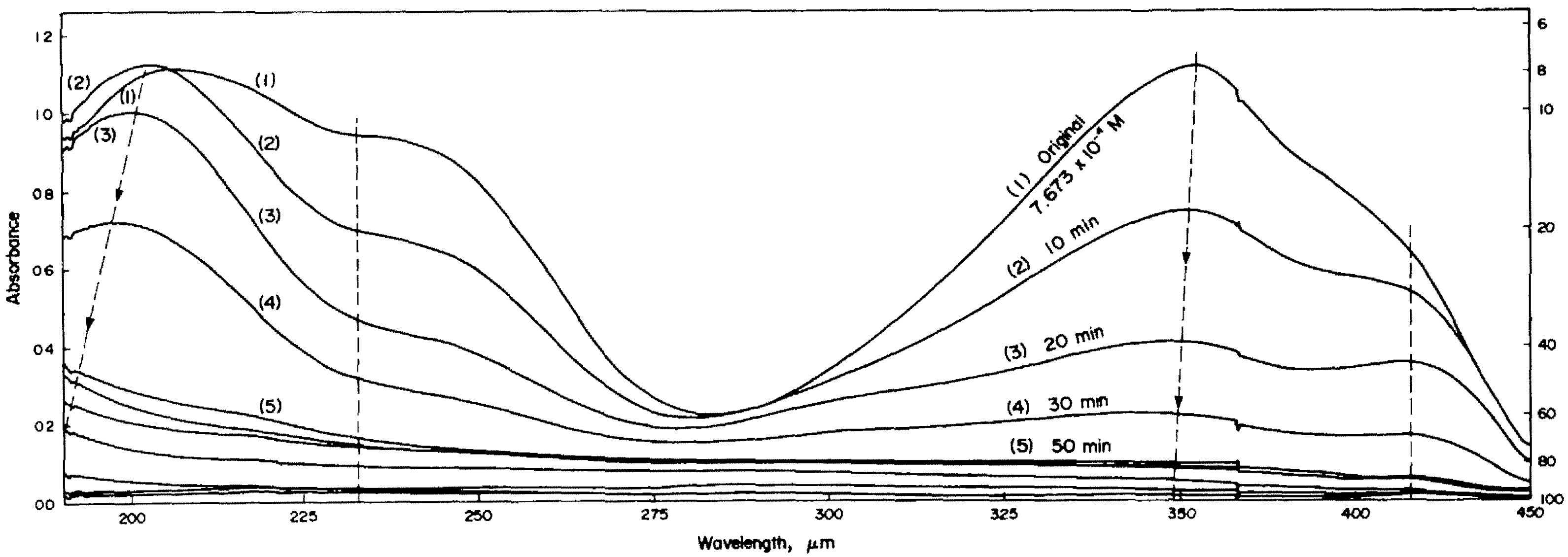

Fig. 1. Absorption spectra of original and irradiated aqueous picric acid solutions (1 mm cells).

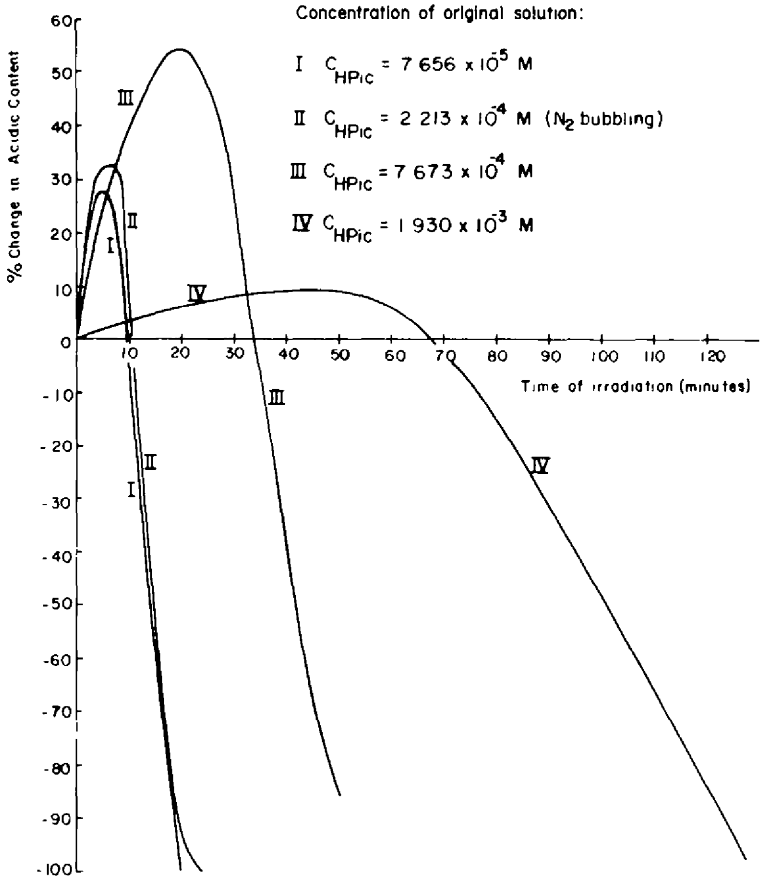

Fig. 2. % Change in acidic content of aqueous picric acid solutions with time of irradiation.

zero, the position of curve IV ($C_{HPic} = 1.930 \times 10^{-3}$ M) relative to the others seems to suggest that at this highest concentration, the HPic solution is more stable towards UV light. This could be explained by the possible screening of some of the attackable monomeric (or such smaller molecular entities) population of HPic molecules by moderately larger aggregates which are thought to be more abundant at such higher concentrations.[1,4]

The change of pH with irradiation-time of solutions of various initial concentrations of HPic and of the other nitrophenols used is consistent with nitro-group elimination, and with the features of the curves in Fig. 1. Comparison of the pH behaviour of *m*- and of *p*-nitrophenol was found interesting. The extent of decomposition of the former seems to exceed that of the latter despite almost equal concentrations. This may confirm tentatively the HNO_2- (or HNO_3)-formation hypothesis inasmuch as $-NO_2$ elimination at the *meta*-position would occur more readily than that at the *para*-position in thermal reactions. As far as the *ortho*-nitro groups are concerned, they might be more difficult to eliminate because of their involvement in intramolecular H-bonds with the neighbouring OH group. This chelation is known to account for the lower solubility and higher volatility of the *ortho*-isomers. The conductance results are also in line with the others and since they would not contribute any further evidence, they are omitted for brevity.

Reverting to the absorption spectra in Fig. 1, one notices that the band in the 350 nm region is suppressed much quicker than that in the 200 nm region, or the shoulder in the 230 nm region. In the meantime, a distinct new band appears in the 410–420 nm region. Other features are a slight blue shift of the 350 nm band and a large one of the 200 nm band.

When the optical density was examined as a function of time of irradiation at each of the wavelengths of 205, 235, 354 and 416 nm, and for each of the two initial concentrations of 4.792×10^{-2} M (I) and 7.673×10^{-3} M (II) HPic, it was found that curves (I) and (II) run more or less parallel to each other in the cases of wavelengths 205 and 416 nm only. At 235 and 354 nm, (II) declines steeply with time throughout the interval from 0 to 30 or 50 min whereas (I) hardly decreases at all over the initial 10 min.

Assignment of the absorption bands and interpretation of these other features may be based conclusively on a knowledge of the photolysis products. Tentatively, the appearance in the intermediate stages of a new band at a longer wavelength (*ca.* 416 nm) may be connected with the observation that in all cases the colour of the photolysed solution changed from the usual greenish yellow through amber, then gradually to colourless. This might be the result of increased conjugation in some stable intermediate entities formed by the association of the produced "dihydroxynitrophenol" with HPic or Pic^- via H-bonding. Jaeckel's polarographic measurements[2] also suggested the formation of some stable intermediate.

The use of purified N_2 as a "carrier gas" and its scrubbing in pure water (with pH monitoring) after leaving the reactor ensured that prior to irradiation, complete expulsion of CO_2 was achieved. The small decrease in the pH of the water sample during the photolysis therefore strengthened the inference that HNO_2 (or HNO_3) is formed as a result of nitrite displacement.

Unfortunately, apart from the brief study by Jaeckel, we have not been able to trace any UV photolysis of these compounds under the conditions of our experiments. However, Gold and Rochester[5] studied the photolysis of picric acid in methanolic sodium methoxide solutions using a tungsten lamp. They explained their results in terms of nitro group elimination leading to nitrite formation.

Their reaction scheme envisages displacement of a nitro-group by OMe in the activated complex. The UV-visible absorption spectra of the original and irradiated HPic solutions, obtained in their study have very close resemblance to ours in aqueous solutions. In both these studies, the acid is present in its ionised form, and hence the reactions related to the photolysis of the picrate ion. Our spectra for the photolysis of *m*- and of *p*-nitrophenol also show similar features.

More recently, Lestinger and Steller[6] found that at wavelengths greater than 290 nm, 10^{-4} M solutions of 4-nitroanisole in aqueous t-butyl alcohol undergo 80% nitrite displacement yielding 4-methoxyphenol or 20% nitrite displacement yielding 4-nitrophenol as the main product. The concentration of OH^- was approximately 1.610^{-2} M. No reaction was observed in the absence of OH^-.

The subject of nucleophilic aromatic photosubstitution has recently been reviewed extensively by Havinga *et al.*[7] Whilst examples of nitrophenol reactions in aqueous solutions were still lacking, these authors have made some useful generalisations, tentative as they ought to be, regarding the specific influences of the leaving group, the nucleophile and the solvent. They also pointed out the contrast between the operation of these factors in the case of photosubstitution and that of analogous thermal reactions. Our present study is inadequate for testing, for instance, the importance of "merging (resonance) stabilisation" as an important factor in determining the path of aromatic photosubstitutions. However our above conclusions from the present circumstantial evidence are further borne out by these authors' generalisations that the nitro group functions well as a leaving group and that OH^- is an efficient nucleophile in nucleophilic aromatic photosubstitution.

Since accurate pK determinations—especially through conductance measurements—are particularly sensitive to both concentration errors and to contamination, the lack of concordance of these data[1] may readily be explained in terms of uncontrolled photolysis.

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