[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Further Photo-oxidations in Rigid Media

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In addition to the photo-oxidations described in previous papers,[1,2,3] we have illuminated a large number of substances to find what classes of substances can be so oxidized. So far we have found the phenomenon only in compounds containing basic nitrogen, sulfur or oxygen.

We have also studied the absorption spectra of the substances produced; for except in the remarkable cases where a single photon produces a two-stage oxidation,[3] all of the products are of the semiquinone type. We are thus able to study the spectra of a large number of odd molecules which are unstable under ordinary conditions, and to obtain material for the eventual formulation of the rules of color in molecules containing an uneven number of electrons. The results will be presented approximately in the order in which they were obtained, proceeding from the more complicated to the simpler molecules.

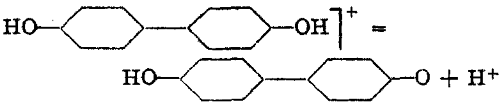
Diarylamines.—We have previously[1] studied triphenylamine, tri-*p*-tolylamine, methyldiphenylamine and diphenylamine. In the last case two products were obtained, one in which only an electron is lost and the other in which both an electron and a proton are lost, which is equivalent to losing one hydrogen atom. Calling the original amine DH, the products are DH^+ and D. In general the substance resulting from the loss of an electron and that produced by the further loss of a proton may be called the odd ion and the radical, respectively.

Similar results were obtained with di-β-naphthylamine. The illuminated sample has a band at 13400 cm.$^{-1}$ (7460 Å.) and another stronger band just beyond the limits of our apparatus, with a maximum at perhaps 8200 Å. Provisionally we ascribe these bands respectively to DH^+ and D. A stable semiquinine form can be obtained at room temperature by oxidizing the amine in concentrated sulfuric acid with lead tetra-acetate. The resulting ion DH_2^{++} has a broad band with a maximum at 14300 cm.$^{-1}$ (7000 Å.). We note, in comparing the DH^+ and D forms with those of diphenylamine, the strong bathochromic effect of replacing phenyl by naphthyl groups. In one experiment with phenyl-β-naphthylamine only one band was found at 13000 cm.$^{-1}$ (7700 Å.). This was probably the D band.

Carbazole, which is the same as diphenylamine except for the linking of two ortho carbons, gave upon illumination a complicated absorption curve with a main peak at 15500 cm.$^{-1}$ (6450 Å.) and with marked resolution of vibrational bands, as was to be expected[4] from its tightly bound structure. This band system, which is probably contributed to by both odd ion and radical forms, has not been analyzed. Sometimes a band was observed at 13670 cm.$^{-1}$ (7310 Å.) which we suspect to be due to the phosphorescent state.[5]

Derivatives of Biphenyl.—Benzidine, tetramethylbenzidine and *sym*-diphenylbenzidine all give ions whose spectra extend into the infrared. The first band maximum, that is, the one appearing at lowest frequency, we found by extrapolation[6] to come at about 11300 cm.$^{-1}$ with the first two substances, and 10000 cm.$^{-1}$ with diphenylbenzidine.

When, replacing the two *p*-amino groups by hydroxyls, we illuminate 4,4'-dihydroxybiphenyl there is a considerable shift to higher frequencies. Here we find the odd ion and can follow the loss of a proton to give the radical, according to the reaction



(1)

Figure 1 shows the spectrum given by 4,4'-dihydroxybiphenyl immediately after illumination and then after slight warming. The peak at 16120 cm.$^{-1}$ (6200 Å.) belongs to the odd ion; the peak at 15400 cm.$^{-1}$ (6490 Å.), gradually built up on standing, to the radical. It is interesting to note that, in spite of the dissymmetry of the radical, this system conforms to the rule that the radical absorbs at lower frequency than the odd ion.

We next illuminated similar compounds with a single para group, namely, *p*-aminobiphenyl and *p*-diethylaminobiphenyl. With the former, the first peak is at 22990 cm.$^{-1}$ (4350 Å.); with the latter at 21780 cm.$^{-1}$ (4590 Å.). With *p*-hydroxybiphenyl the first peak was found to be too far into the ultraviolet to measure. Here the ordinary rules of color prevail, namely, a dialkylamino group is a stronger auxochrome than the amino, which in turn is a much stronger auxochrome than hydroxyl.

Derivatives of Benzene.—*p*-Phenylenediamine and its various N-methyl derivatives can be oxidized at room temperature and give odd ions which, under proper conditions, are sufficiently stable for spectrophotometric study. We owe to the careful work of Michaelis, Schubert and

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(1) Lewis and Lipkin, THIS JOURNAL, **64**, 2801 (1942).

(2) Lewis and Bigeleisen, *ibid.*, **65**, 520 (1943).

(3) Lewis and Bigeleisen, *ibid.*, **65**, 2419 (1943).

(4) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(5) In the three cases in which the absorption of the phosphorescent state has been studied, fluorescein (Lewis, Lipkin and Magel, THIS JOURNAL, **63**, 3005 (1941)), crystal violet (Lewis, Magel and Lipkin, *ibid.*, **64**, 1774 (1942)), and diphenylamine,[1] the first and third had phosphorescent half-lives of the order of 1 second, crystal violet of 0.01 second. In the present case the half-life is many seconds. This in turn is short compared with the half-life of solutions of the lithium salts of carbazole and diphenylamine. In the last case the half-life at liquid air temperature is about an hour.

(6) Lewis and Bigeleisen, ref. 3.

Granick[7] a knowledge of these conditions and of the absorption spectra. Except for extremely small shifts due to change of solvent and temperature, we obtained identical absorption curves by photo-oxidation. Their work showed the very large effect in these compounds of substituting methyl for hydrogen on the nitrogens. Each substitution of hydrogen by methyl caused an increase in $\lambda_{\max.}$ of about 300 Å.

It seemed of interest to attempt the photo-oxidation of *m*-phenylenediamine. In molecules with an even number of electrons very little resonance is to be expected between two similar groups meta to one another, but it seemed doubtful whether such rules would apply to odd molecules. In fact, although light of high frequency was required for its oxidation, *m*-phenylenediamine gave an odd ion whose absorption curve was entirely similar to that of the odd ion of *p*-phenylenediamine and at only a little higher frequency. A very sharp maximum was found at 20690 cm.$^{-1}$ (4830 Å.) with a second maximum nearly as high at 22170 cm.$^{-1}$ (4510 Å.).

An absolutely identical spectrum was found for 2,4-diaminotoluene, showing what had already been brought out in the work of Michaelis, Schubert and Granick[7] that there is no appreciable steric effect when a single methyl group is ortho to an unsubstituted amino group.[8]

When we replace the amino groups of *p*-phenylenediamine successively by methoxy groups we find progressive increase in the frequency of the first band maximum as shown in Table I. The next three substances in the table, hydroxy compounds, namely, *p*-aminophenol, hydroquinone, and *p*-hydroxythiophenol, may suffer the loss of a proton, so that the values given in the table may belong to the radical rather than to the odd ion, in which case $\bar{\nu}_{\max.}$ for the odd ion will be found at a higher frequency.

It was not supposed at first that so simple a compound as aniline itself would suffer photo-oxidation, or, if it did, would give a band within the reach of our apparatus. However, with high frequency illumination (2700 Å.) we were able to obtain a band for the odd ion at 25890 cm.$^{-1}$ (3860 Å.). The frequency of the band is greatly diminished when we go to dimethylaniline. This change is comparable with the similar changes in the Wurster series. A still more remarkable shift is found in the case of *p*-toluidine, where the para methyl group has produced a bathochromic shift of 500 Å. All these remarkable auxochromic effects can best be explained by assuming that, in these small molecules, the small penetration of resonance (electron cloud) into the methyl group is enough to increase greatly the polarizability of the molecule.

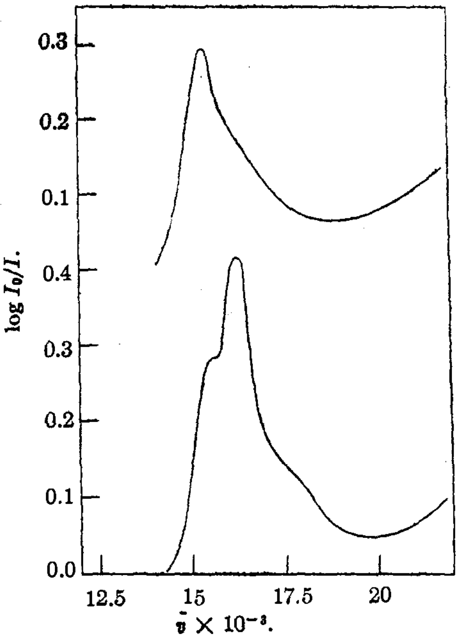

Fig. 1.—Absorption curves of the products of illumination of 4,4′-dihydroxybiphenyl: lower curve immediately after illumination at 90°K; upper curve after forty-five minutes at about 110°K.

With phenol no observable effect of illumination was expected or found. However, with thiophenol a band appeared at the same place as that of aniline but here again we have not yet learned whether this belongs to the odd ion or the radical. Also α- and β-naphthol on illumination show color due to broad bands, or complicated band systems beginning at about 5300 Å.

TABLE I

THE FIRST ABSORPTION MAXIMA OF THE ODD IONS OF SUBSTITUTED BENZENES

Substituents	$\bar{\nu}$, cm.$^{-1}$	λ, Å.
1,4-Tetramethyldiamino	16030	6240
1,4-Diamino	20030	4990
1,3-Diamino	20690	4830
1-Methyl-2,4-diamino	20690	4830
1-Amino-4-methoxy	22170	4510
1,4-Dimethoxy	23880	4190
1-Amino-4-hydroxy[a]	22410	4460
1,4-Dihydroxy[a]	24340	4110
1-Hydroxy-4-mercapto[a]	18800	5320
1-Methyl-4-amino	22990	4350
Amino	25890	3860
Dimethylamino	21780	4590
Mercapto[a]	25890	3860

[a] These values may be for the radical rather than the odd ion.

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[7] Michaelis, Schubert and Granick, THIS JOURNAL, 61, 1981 (1939).

[8] The Referee suggests that on account of the remarkable result with *m*-phenylenediamine the possibility of contamination with the para compound should be discussed. Our *m*-phenylenediamine was not so carefully purified as the 2,4-diaminotoluene which was twice sublimed in a very high vacuum. The curves for both substances were identical. The sublimation might not remove all traces of the ortho and para compounds but their absorption maxima come at a different place and the observed maxima are so sharp that the presence of a few per cent. of the para compound would be immediately detected. Furthermore the meta compounds are distinguished by the high frequency of light required for photo-oxidation.

Ethers and Ketones.—4,4′-Diaminodiphenyl ether was photo-oxidized at moderate frequency giving a band at 22740 cm.$^{-1}$ (4400 Å.). So also Michler's ketone gives a band at 19700 cm.$^{-1}$ (5070 Å.). It is evident from the examples here given that the number and variety of the odd ions that can be produced by photo-oxidation, and studied spectroscopically, can be indefinitely extended. Except in rare cases these semiquinone forms cannot be studied under ordinary conditions of solvent and temperature. Many of them can, however, be obtained by photo-oxidation at higher temperatures, in a sufficiently rigid solvent such as glycerol or triethanolamine at −80°. Even at room temperature they may be observed in supercooled dextrose, although it is difficult to melt the dextrose and dissolve the solute without a slight caramelization which causes absorption in the near ultraviolet and the violet.

It is not to be supposed that photo-oxidation occurs more often in rigid than in ordinary media. However, in a fluid medium the electron can return in a very short time. Nevertheless, in the fluid medium during this short time in which the electron is removed, other processes may occur which lead to the decomposition of the original substances. Most of the substances discussed in this paper must be kept in dark bottles, and it seems probable that in their photo-chemical decomposition, the initial process is the ejection of an electron. On the other hand, in the gaseous state, where, because of the low dielectric constant, the energy required for the ejection of an electron is much greater, it would take light of very high frequency to cause such an ejection.

Summary

A further study is made of the odd ions and radicals produced by the illumination of many types of organic substances in a rigid solvent. The spectra of these substances have been determined with a view to the ultimate formulation of the laws of color in odd molecules. That these laws are different from those for ordinary molecules is shown by the color of the odd ion of *m*-phenylenediamine and perhaps by the remarkable auxochrome effects found in substituted benzenes. The role of electron ejection in ordinary photochemical processes is discussed.

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The Vapor Phase Nitration of Toluene

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In a previous report[1] it was shown that the vapor phase nitration of toluene by means of 70% nitric acid proceeded in the neighborhood of 150° with the formation of ortho, meta and para-nitrotoluenes in somewhat different proportions than are recorded for the liquid phase nitration. Specifically, Holleman and others[2] obtained in the liquid phase at 30° values of 58.8% ortho, 4.4% meta and 36.8% para, while the reaction in the vapor phase at 150° gave 55.8% ortho, 5.0% meta and 39.2% para.

The present study is an extension of the previous work under varying experimental conditions to determine in particular the effect of changes in temperature and of concentration of nitric acid on the relative proportions of the three isomers. In addition the analytical results obtained previously have been checked by subjecting the present mixtures to two other independent methods of analysis.

Experiments have been carried out in which the concentration of the nitric acid was varied from 70 to 90%, the amounts being adjusted so that the ratio of nitric acid to toluene remained constant. This variation caused an increase in the over-all conversion to mononitrotoluene from 39 to 74%, but had only a slight effect on the ratio of the isomers. Some tendency toward an increased percentage of the para compound was noted.

Holleman and Van den Arend[3] have observed that a change in temperature from −30 to +60° in the liquid phase nitration causes a decrease in the percentage of *p*-nitrotoluene formed. In the present series of experiments the temperature in the vapor phase nitration was varied between 150 and 350° to discover the effect of temperature change on the isomer ratio in the gas phase reaction. Since a greater tendency for oxidation and other side reactions, which might have upset the true isomer ratios, was encountered at the higher temperatures and also to a less extent at the higher acid concentrations, a program of identification and analysis of the by-products was carried out. Using 70% nitric acid it was found that proportion of the by-products to the mononitrotoluene was so high as to make specification of the isomer ratios unreliable above 250°. In the range 150 to 250°, the observed change in the isomer ratio was noted to be within the range of experimental error, indicating that the rates of gaseous nitration have similar temperature coefficients.

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[1] J. L. Bullock and E. T. Mitchell, THIS JOURNAL, **63**, 3230 (1941).

[2] (a) A. F. Holleman, *Rec. trav. chim.*, **18**, 268 (1899); **33**, 1 (1914); (b) C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931).

[3] A. F. Holleman and M. J. Van den Arend, *Rec. trav. chim.*, **28**, 408 (1909).