

strength of the "normal" phosphorescence. Thus, the amines give much brighter light emission than the corresponding ethers or phenols, and the metal derivatives are more brilliant than their parent acids. The most marked effects are found with the strongly phosphorescent aromatic lithium amides, which, in dry form, are instantly destroyed when exposed to air.

The nature of the solvent has a marked effect on the intensity of delayed luminescence. Thus, carbazole gives a much more intense luminescence in EPT than in EPA, and in the latter solvent, diphenyl ether and hydroquinone show no delayed luminescence at all. In this and similar cases, the amine solvent may afford better electron traps and thus enhance the luminescence. If the solvent is very basic negative ions may be formed (naphtholate, phenolate) which are more readily oxidized than the uncharged molecule. In addition, the neutral radical resulting from photooxidation of a negative

ion exerts no long range coulomb attraction on the electron, and thus even shallow solvent traps suffice to prevent immediate recombination.

In radiation chemistry the formation of triplet states by ion-electron or radical-electron recombination frequently has been assumed. Such processes, which are undoubtedly widespread, may be directly observed in these luminescent systems. Attempts have been made to identify ions and especially solvated electrons produced by X-irradiation of rigid amine solvents like EPT.²¹ The results so far have been negative, possibly because the available traps were insufficiently deep to hold the electron against coulombic restoring forces. Similar negative results were obtained by Roberts and Allen²² who looked for solvated electrons in irradiated liquid ammonia.

(21) These experiments were carried out by Dr. H. Rubin.

(22) R. Roberts and A. O. Allen, *THIS JOURNAL*, **75**, 1256 (1953).
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

Symmetrical Semiquinone Formation by Reversible Photooxidation and Photo-reduction¹

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RECEIVED MAY 19, 1954

In rigid solvents the illumination of *either* diphenyl-*p*-phenylenediamine *or* the corresponding imine yields a new substance having a characteristic absorption band at 7100 Å. It is shown that this compound is the semiquinone of the imine-amine oxidation-reduction couple. Thus, both photooxidation and the inverse process of photo-reduction may occur, leading to the same semiquinone. Similar behavior is demonstrated for the hydroquinone-benzoquinone couple.

We have previously described experiments in which were demonstrated the formation of radicals and solvated electrons by illumination of readily oxidized organic molecules in rigid solvents.² This process of direct photooxidation may be used to prepare a wide variety of semiquinones, as has been shown by Lewis and his school.^{3,4} The radical or radical-ion remaining after electron ejection may then undergo a proton-transfer reaction on standing, to yield the ionic form of the semiquinone which is most stable in the given solvent.

In this paper, again using the rigid solvent technique to stabilize high energy intermediates, we show that the inverse process of *photo-reduction* also occurs under suitable conditions, and that the same semiquinone may be prepared by irradiating *either* the fully oxidized or fully reduced form of a given oxidation-reduction couple. For example, the irradiation in rigid solvents of either diphenyl-*p*-phenylene diamine or the corresponding imine produces a characteristic blue color. This same blue compound is obtained by chemical oxidation of the amine or reduction of the imine and its mode of preparation, oxidation-reduction titration and para-

magnetism establish that it is the semiquinone (probably the doubly protonated form, RH_2^+) of the imine-amine couple.

The oxidation-reduction system hydroquinone-benzoquinone also yields the same spectrum when either the reduced or oxidized form is irradiated in rigid solution, in complete analogy with the behavior of the imine-amine couple. The new spectrum is therefore attributed to the semiquinone of hydroquinone.

Just as in reversible photooxidation, softening of the photoreduced solution by warming restores the original spectrum.

Experimental

1. **Spectra.**—Absorption spectra at room temperature were taken with a Beckman Model DU quartz spectrophotometer. For low temperature work, a specially modified Beckman was used. The cell compartment of this instrument was replaced by a larger box and frame, holding an unsilvered Dewar. This was either a large Pyrex vessel, made from tubing selected for good optical quality or a smaller quartz flask, carrying four plane windows. Cylindrical dural-block thermostats, with dural extension rods dipping into liquid nitrogen and resting on the bottom of the flasks, were made to fit the dewars. The thermostat blocks carried vertical slots for holding the absorption cells and horizontal holes to permit passage of the light beam. Sectors were also cut out for addition of liquid nitrogen. By rotation of a vertical axial shaft, fixed to the thermostat block, either cell could be brought into the light beam. Adjustable pins, mounted on the shaft and striking a stop fixed to the frame, enabled the cells to be oriented precisely and reproducibly. Lateral motion of the cells was minimized by fitting the thermostat closely within the dewar

(1) This research is supported by grants from the U. S. Atomic Energy Commission (Contract No. AT(30-1)-820). Material in this paper is taken in part from the doctoral thesis of J. Rennert (Department of Chemistry, Syracuse University, February, 1953).

(2) H. Linschitz, M. G. Berry and D. Schweitzer, *THIS JOURNAL*, **76**, 5833 (1954).

(3) G. N. Lewis and D. Lipkin, *ibid.*, **64**, 2801 (1942).

(4) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 520, 2419, 2424 (1943).

and holding the upper end of the shaft in a bearing in the (removable) upper cross-member of the frame. A small blower was set into the side of the cell compartment to prevent sweating of the dewar. To help define the beam, a 1-mm. slit, formed by cementing two razor blades to an adjustable holder, was mounted immediately in front of the dewar. The nitrogen level was maintained below the cells, to avoid interference with the light beam, and by varying this level the temperature of the thermostat block and thereby the rigidity of the glass was conveniently adjustable. In many experiments in which temperature control was not critical a simpler cell-holder was used. This consisted of two $3/8$ " dural discs, held $1\frac{1}{8}$ " apart by four dural rods. Holes were bored in the upper disc to support the cells. The lower disc again carried a dural extension rod, resting on the dewar bottom and immersed in nitrogen, and the assembly was fixed to an axial shaft supported in the upper bearing. With either of these arrangements, transmission measurements could readily be reproduced to 0.5%.

2. Materials.—Diphenyl-*p*-phenylenediamine (Eastman Kodak Co.) was crystallized several times from benzene. The corresponding imine was prepared by chromic acid oxidation of the amine in glacial acetic acid, after the method of Piccard,⁵ and recrystallized from ethanol. Benzoquinone was recrystallized from purified ligroin and vacuum-sublimed. Solvents were purified as described previously.² "EPA" solvent was a mixture of ether, isopentane and ethanol, in 8:3:5 ratio. "EPT" was ether, isopentane and triethylamine, in 5:5:2 ratio.

3. Preparation of Semiquinone of Diphenyl-*p*-phenylenediamine.—Qualitatively, the spectra produced by treating the imine with stannous chloride in acetic acid, or by treating the amine with ferric ion, bromine or benzoyl peroxide in acetic acid all agreed. Spectrophotometric titration of the amine with ferric ion in ethanol showed that the absorption at 7100 Å. reached a maximum at a ratio of amine/Fe⁺⁺⁺ = 1.0. Similar results were obtained by titrating the imine

with Sn⁺⁺, for which the 7100 Å. absorption leveled off at a ratio of imine/Sn⁺⁺ = 2.0. However, the extinction coefficients computed for the semiquinone prepared by these methods did not agree. The differences are ascribed to simultaneous occurrence of the second step of the reaction, incomplete reduction by Sn⁺⁺ (some time was required to develop the color) and other side reactions causing fading. A safer method for establishing the stoichiometry and the extinction coefficients appeared to be the titration of the imine by the amine itself. A number of preliminary experiments carried out to find the best conditions for forming the semiquinone quickly and at the same time stabilizing it in solution led to the following simple technique. Solutions of imine and amine were prepared in ethanol which had been boiled under aspiration. Five-ml. portions of the imine solution were pipetted into a series of 50-ml. volumetric flasks, various measured amounts of the amine solution added from a buret, and the flasks filled with additional boiled ethanol. Samples were then taken, acidified with equal volumes of boiled glacial acetic acid to develop the color and immediately measured in the Beckman spectrophotometer. Under these conditions, the rate of fading was sufficiently slow to permit fairly precise determinations of optical density.

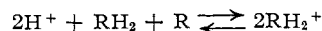
4. Paramagnetic Resonance Measurements.—These were carried out in collaboration with Prof. S. I. Weissman, of Washington University, using apparatus previously described.⁶ For these measurements, the semiquinone was prepared essentially as described above, by adding acetic acid to an ethanol solution containing amine and imine in equimolar quantities. If the solution is too concentrated, a green color, which may be due to a dimer, is obtained and the solution shows no paramagnetic behavior. Simple dilution, even with water, develops the characteristic clear blue of the semiquinone. The solution, contained in a glass capillary, was then inserted in the wave guide for measurement. The radical (sulfate) may be readily obtained in solid form by adding a drop of sulfuric acid to an equimolar solution of imine and amine in ether. A heavy blue precipitate immediately forms which is then centrifuged and washed with ether. The crystals are paramagnetic.

5. Photochemical Procedure.—Solutions of substrates were prepared in suitable mixed solvents, placed in absorption cells, degassed on the vacuum line and sealed off. Pyrex cells were made of 6 mm. square tubing. Quartz cells were 2 × 8 mm. in cross-section, and attached to Pyrex through graded seals. Irradiations were carried out at liquid nitrogen temperature, using a G.E. AH-6 mercury arc.

Results and Discussion

Figure 1 shows typical absorption spectra obtained by reducing diphenyl-*p*-phenylenediamine with stannous chloride, or by oxidizing the amine with benzoyl peroxide, both in glacial acetic acid. Since the solutions are rather unstable no quantitative discussion is attempted, but the qualitative features of the spectra are identical in the two cases, with peaks at 7100 and 3900 Å. On standing, these peaks fade at the same rate and therefore are ascribed to the same species.

The results of a titration of imine with amine, carried out as described above, are given in Table I. From values of the optical density in solutions containing large excess of amine the extinction coefficient for the semiquinone at 7100 Å. was found to be 1.37×10^4 assuming the reaction to be



Equilibrium constants for this reaction are also given in Table I, the hydrogen ion activity in 50% ethanol-acetic acid being incorporated into K . Since the equilibrium concentrations of imine and

(6) J. Townsend, S. I. Weissman and G. E. Pake, *Phys. Rev.*, **89**, 606 (1953); T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissman, *J. Phys. Chem.*, **57**, 804 (1953); It is a pleasure to thank Prof. Weissman for his assistance and hospitality during the course of these measurements.

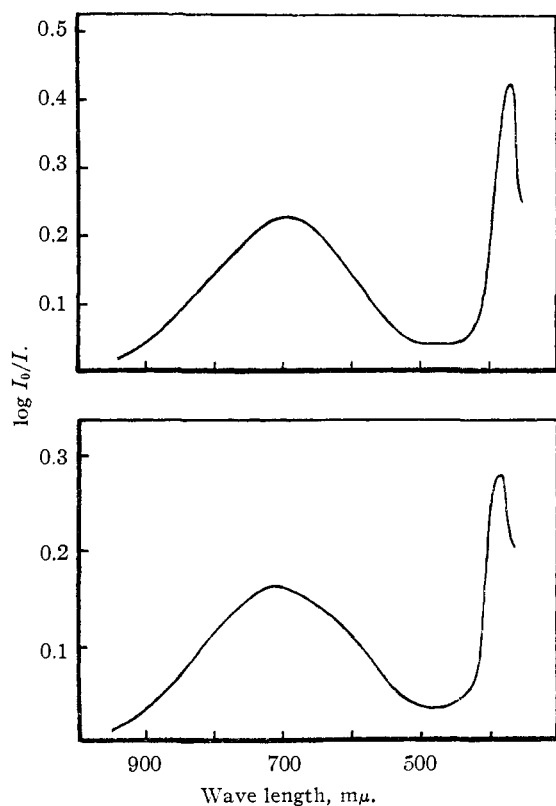


Fig. 1.—Absorption spectra of reduced diphenyl-*p*-phenylenediamine and oxidized diphenyl-*p*-phenylenediamine: upper curve, mixture of imine and SnCl₂; lower curve, amine and benzoyl peroxide; solvent, acetic acid.

(5) J. Piccard, *Ber.*, **46**, 1835 (1913).

amine are obtained by difference the value of K is very sensitive to small experimental errors, particularly near either end of the titration. The relative constancy of K (between points 3-11) while the equilibrium ratio $[I]/[A]$ is varied over 400-fold justifies the assumed stoichiometry. Potentiometric titrations of diphenyl-*p*-phenylenediamine, performed by Michaelis and Hill⁷ have shown previously that one-step oxidations were involved.

TABLE I
SPECTROPHOTOMETRIC TITRATION OF DIPHENYL-*p*-PHENYLEDIIMINE WITH AMINE

Initial imine concn., $1.82 \times 10^{-6} M$; initial amine concn. (stock solution), $3.51 \times 10^{-4} M$; total volume, 100 ml.; solvent, 50% ethanol-acetic acid; molar extinction coefficient of semiquinone, 1.37×10^4 .

Solution	Amine, ml.	Optical density $\log_{10} I_0/I$ ($\lambda = 7100 \text{ \AA.}$)	$([I]/[A])_{eq.}$	K
1	1.62	0.169
2	2.60	.243	36	130
3	3.71	.316	4.5	54
4	4.78	.373	1.46	51
5	5.09	.386	1.09	51
6	5.65	.411	0.66	58
7	7.46	.424	.25	33
8	9.99	.449	.097	32
9	13.06	.463	.045	30
10	17.25	.472	.022	28
11	25.35	.487	.006	41
12	41.54	.494	.0013	60

Further proof of the semiquinonoid character of the blue intermediate is found in the paramagnetic resonance absorption of solutions containing this

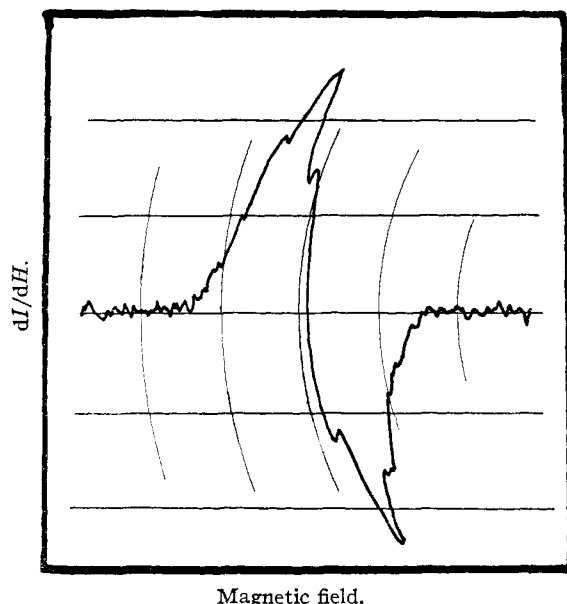


Fig. 2.—Paramagnetic resonance absorption spectrum of 1:1 imine-amine solution in ethanol-acetic acid solvent. Derivative of micro-wave absorption vs. magnetic field; frequency, 9000 mc.; field at center of pattern, 3200 oersteds; hyperfine splitting between components, about 7 oersteds.

(7) L. Michaelis and E. S. Hill, *THIS JOURNAL*, **55**, 1488 (1933).

compound. The spectrum obtained at about 9000 mc. and 3000 gauss shows, in addition, hyperfine structure,⁶ five peaks being clearly resolved (Fig. 2). Interpretations of this structure will be offered elsewhere.

The effects of light on the imine and amine in rigid solution are given in Fig. 3. The identity of the photo-products with the intermediate of Fig. 1 is evident. Irradiation of the amine leads immediately to the formation of the new spectrum. On the other hand, the bands at 7100 and 3900 Å. build up only gradually in irradiated solutions of the imine when the glass is allowed to stand at low temperature for about an hour following exposure to light. These observations are consistent with the assignment of the new spectrum to the doubly protonated form, RH_2^+ , of the (acid-stabilized) semiquinone. Thus, electron-ejection from the amine results directly in RH_2^+ , whereas proton-transfer must occur following photoreduction of the imine. Slow color development following photo-oxidation has been observed previously.^{3,4} Attempts to prepare other ionic forms of the semiquinone by irradiating the imine in basic solvent (EPT) led only to its irreversible destruction.

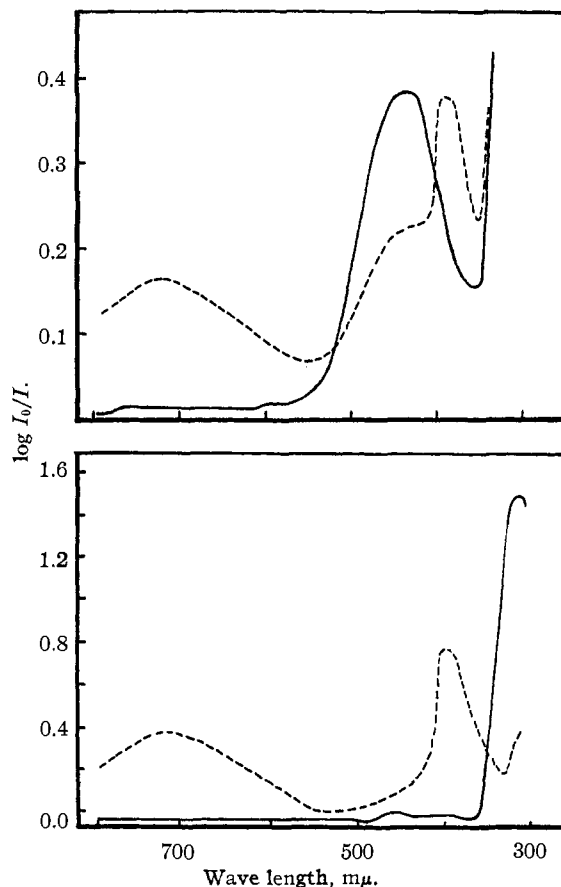


Fig. 3.—Reversible semiquinone formation by photo-reduction of diphenyl-*p*-phenylenediimine (upper figure) and photo-oxidation of diphenyl-*p*-phenylenediamine (lower figure), in rigid EPA solvent. Solid lines are original and final (after warming and refreezing) spectra; dashed lines, after illumination with AH-6 arc; imine, $4.4 \times 10^{-6} M$ in Pyrex cell; amine, $1.1 \times 10^{-4} M$ in quartz cell.

Irradiating either hydroquinone (EPT) or benzoquinone (EPA) leads to formation of a new absorption peak at 4140 Å. (Fig. 4). This band has been previously obtained by Lewis and Bigeleisen,⁴ by

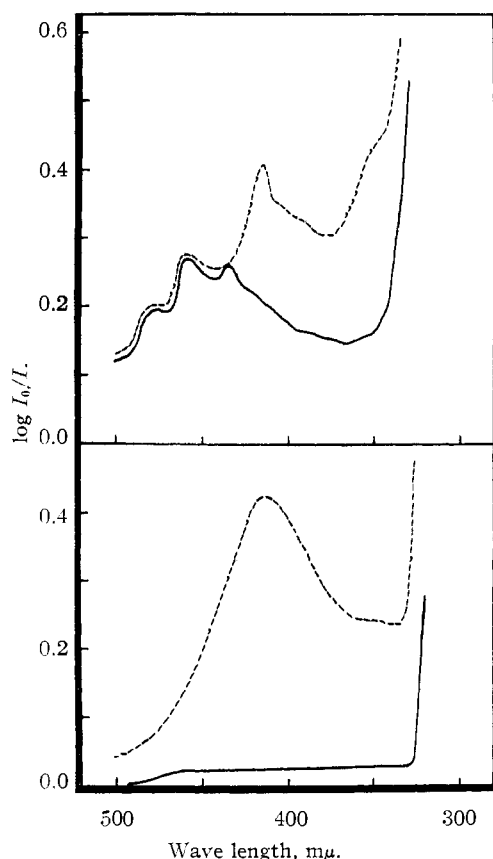


Fig. 4.—Reversible light-induced changes in absorption spectra of quinone (upper figure) and hydroquinone (lower figure). Solid lines are original spectra; dashed lines, after irradiation. Quinone, 0.011 *M* in rigid EPA, irradiated with 1000-watt tungsten lamp through Corning filter No. 3384; hydroquinone, 7.3×10^{-3} *M* in rigid EPT, irradiated with AH-6 arc in quartz.

the photooxidation of hydroquinone in EPA. The formation of the band by photoreduction of benzoquinone in EPA is facilitated by adding traces of triethylamine to the solvent. Here there are no marked effects on standing and we believe that the 4140 peak is due to the unprotonated, negatively charged ion of the semiquinone. In this case, however, the situation is complicated by another band appearing as a shoulder in the irradiated quinone spectrum at about 3550 Å. Both 3550 and 4140 Å. bands disappear when the irradiated solution is softened. The exact assignment of the spectra is still uncertain.

Photo-reduction, as demonstrated in these experiments, presumably occurs by removal of electrons or hydrogen atoms from the solvent by the excited oxidant, the oxidation-reduction potential of the oxidant being altered in the excited state. The alternative to this is the assumption that the absorption itself arises from an "electron-transfer" transition of the type described by Mulliken.⁸ However, neither the visible nor near ultraviolet absorption bands of benzoquinone, both of which are photochemically active in the solvents used here, arise from this latter type of transition.^{9,10} The same question may be raised regarding the mechanism of photooxidation, whether it proceeds by direct photo-ejection or by chemical reaction between the excited reductant and solvent. In those cases in which one can demonstrate the presence of trapped electrons in the solvent,² simple ejection would appear to be the preferable mechanism. Even here, loss of the electron may occur only after a number of molecular vibrations, permitting radiationless transitions out of the initially excited state into one which interacts more strongly with the ionic state. The formation of triplets upon recombination of radicals and electrons² suggests that this may also be the path of photo-ionization.

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(8) Mulliken, *THIS JOURNAL*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(9) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(10) S. Nagakura and A. Kuboyama, *THIS JOURNAL*, **74**, 1003 (1954).