"Polymerization" of N,N′-Diphenyl-*p*,*p*′-diphenoquinonimine

BERNHARD SEIDEL AND GEORGE S. HAMMOND

Contribution No. 2912 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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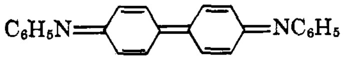
In the course of a related study[1] we observed that N,N′-diphenyl-*p*,*p*′-diphenoquinonimine, I, henceforth referred to as Q, undergoes a reaction, probably polymerization, in acetic acid solution. Preliminary characterization of the product has been carried out and the kinetics of the process have been studied.

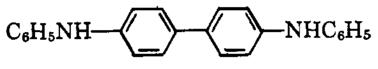
Results

The reactions were studied in solvents consisting of glacial acetic acid to which varying amounts of 100% sulfuric acid were added. The quinonimine, Q, was generated by oxidation of QH_2 with potassium dichromate dissolved in acetic acid. Unless air was rigorously excluded from the reaction mixture, kinetic measurements were not at all reproducible; reproducibility was not very good under even the most aseptic conditions that we have used.

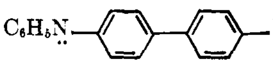
Spectra of the Monomeric Species.—The spectrum of N,N′-diphenylbenzidine has a maximum at 323 mμ (ε 43,900 ± 1.5%) in acetic acid or in dioxane. The band is obviously due to unprotonated QH_2. In stronger acid the 323 maximum disappears and a new maximum appears at 250 mμ. This band has ϵ_{max} 25,500 ± 2% in either acetic acid containing 0.1865 *M* sulfuric acid or in concentrated sulfuric acid and must be due to the second conjugate acid, QH_4^{+2}. The value of K_b[1] for QH_2 has been reported as 2×10^{-14}.[2] No attempt was made to evaluate the second basicity constant because the 250-mμ maximum occurs close to the region in which acetic acid becomes opaque because of end absorption.



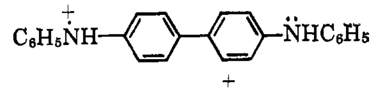
I (Q)



II (QH_2)



III (QH·)



IV ($QH_2\cdot^+$)

Addition of two or more equivalents of dichromate to strongly acidic solutions of QH_2 produces a species which has an absorption maximum at 580 mμ (ε 54,500 ± 1.5%). A second band has a maximum of 390 mμ (ε 9400 ± 2% in 0.1865 *M* sulfuric acid). Solutions of lower acidity were too unstable for accurate measurements; however, a new band with a maximum at about 615 mμ was observed and absorption at 390 mμ was decreased at lower acid concentrations. The maximum at 615 mμ must be attributed to Q, QH^+, or a mixture of the two species.

Addition of one equivalent of dichromate to QH_2 should produce the semiquinonimine (III, QH·). Partial oxidation in media of low acidity produces a new absorption band with a maximum at 460–480 mμ. However, partial oxidation in solutions containing more than 0.0327 *M* sulfuric acid (H_0, 1.07), does not result in appearance of the 460–480-mμ band; spectra show only bands attributed to QH_4^{+2} and QH_2^{+2}. The results imply that the symmetrical, first conjugate acid of the semiquinonimine, $QH_2\cdot^+$ is stable in media of moderate acidity. Increasing the acidity of the medium causes disproportionation to Q and QH_2, both of which form stable second conjugate acids.

$$2H^+ + 2QH_2\cdot^+ \overset{K}{\rightleftharpoons} QH_4^{+2} + QH_2^{+2} \qquad (1)$$

Two other disproportionation reactions can be formulated involving one proton and the conjugate acids QH_3^+ and QH^+. The data shown in Table I have been fitted roughly to equilibrium 1. The value of − log *K* obtained is about 0.6 if the hydrogen ion activity is calculated in terms of H_0. It is clear that improvement in the fit could be obtained by introduction of the two equations involving one proton; however, the data are too limited to justify such an extension.

TABLE I

DISPROPORTIONATION OF QH· IN ACETIC ACID SOLUTIONS CONTAINING VARYING AMOUNTS OF SULFURIC ACID AT 27°

K_c[a]	[H_2SO_4]	H_0[b]	$2H_0$ + log K_c
0.168	0.00052	0.73	0.68
1.04	0.00157	0.25	0.52
24.4	0.00653	−0.36	0.67

[a] $K_c = [QH_4^{+2}][QH_2^{+2}]/[QH_2\cdot^+]^2$. [b] See ref. 3.

The "Polymer."—The color of solutions containing Q, QH^+, and QH_2^{+2} fades at various rates, ultimately producing solutions which have spectra indistinguishable from those containing QH_2. In a number of instances amorphous products separated from the solutions after several days. The greenish "polymers" were insoluble in most solvents but could be partially dissolved in dimethylformamide. The solid samples contained unpaired electrons since they always gave strong electron paramagnetic resonance signals. Addition of potassium dichromate to solutions in which the long wave-length absorption had disappeared resulted in partial, but not complete, recall of the absorption at 580 mμ.

Kinetics of Polymerization.—The disappearance of absorption at 580 mμ was used as a measure of the rate of disappearance of Q. The series of spectra taken in a typical run are shown in Fig. 1. The rate of the reaction is strongly depressed by increasing the concentration of sulfuric acid. Documentation of the kinetic order of the reaction is imprecise. At high acidities the data do not give a good fit to the rate law based upon first order dependence on the concentration of QH_2^{+2}. At intermediate acidities the kinetics usually fit the

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(1) G. S. Hammond, B. Seidel, and R. E. Pincock, *J. Org. Chem.*, **28**, 3275 (1963).

(2) I. M. Kolthoff and L. A. Sarver, *J. Am. Chem. Soc.*, **52**, 4179 (1930).

TABLE II

RATE OF DISAPPEARANCE OF N,N′-DIPHENYL-*p*,*p*′-DIPHENOQUINONIMINE IN ACETIC ACID AT 27°.

Run	Molarity of H_2SO_4	Equiv. $K_2Cr_2O_7$/ equiv. QH_2	$k_1^a \times 10^6$ sec.$^{-1}$	Remarks^b
72-8	0.368	1.00	4.3	Speed up
72-9	.368	2.00	3.3	Speed up
70-1	.212	2.00	4.6	Speed up
70-2	.0425	2.00	23	Not followed beyond 39%
72-6	.0327	0.50	31	Speed up after 50%
72-7	.0327	2.00	24	Speed up after 50%
72-5	.00653	1.00	57	Good fit to 50%
72-4	.00653	4.00	108	Good fit to 78%
70-3	.0065	2.00	77	Good fit to 70%
70-4	.0026	2.00	212	Good fit to 80%
72-14	.00157	0.50	460	Good fit to 80%
70-4a	.00156	0.67	283	Good fit to 67%
72-15	.00157	0.75	348	Good fit to 75%
72-1	.00157	1.00	328	Speeds up after 30%; fits second order to ~70%
72-16	.00157	1.00	468	Badly scattered
72-17	.00157	2.00	398	Speed up after 30%; second order fits with scatter to 80%
70-4b	.00156	1.00	295	Good fit to 75%
72-18	.00157	3.00	421	Fits with scatter to 50%
72-2	.00052	1.00	950	Speed up throughout run; fits second order to 80%
70-5	.00052	2.00	783	Speed up after 30%; fits second order to 85%

[a] Taken from initial tangents to first-order plots in those runs in which data do not fit first-order law. [b] Remarks refer primarily to plots of data according to first-order law.

first-order rate law fairly well within a run but the agreement of calculated values of first-order rate constants for different runs is not really adequate. At very low acid concentrations, the rates of polymerization are very fast and fit the second-order rate law better than the first-order law. Since the data are not clear-cut, Table II summarizes all of the information gathered with deletion of data for runs which were either poorly monitored or rejected on other well defined experimental grounds.

In order to gain some quantitative picture of the dependence of rates on the acidity of the various solutions, we have compared all of the data included in Table II using initial rates expressed as first-order rate constants. Data for runs involving the same acid concentrations have been averaged. Figure 2 shows a plot of log k_1 against the Hammett acidity function, H_0, for the various solutions; the values of H_0 are interpolated from data in the literature[3] for the acetic acid–sulfuric acid system. A line of slope +1.0 has been drawn arbitrarily through the experimental points in Fig. 2. The fact that a tolerable looking fit is obtained implies that the reaction rates are close to being inversely proportional to the hydrogen ion activity. As is indicated by the broken line in Fig. 2, a concave function would improve the fit of the averaged experimental data. However, we are able to make no better sense out of such a correlation than we can from a poor linear relationship.

The effects of variation in amount of dichromate used in the oxidation of QH_2 to Q also were studied. The rate constants were essentially the same in solutions containing residual QH_2 (under oxidation), in those in which the stoichiometric amount was added, and in solutions to which a two- or threefold excess of dichromate had been added. Representative data are included in Table II. Addition of excess dichromate does not change the absorbance due to Q and its conjugate acids. However, the excess dichromate must be destroyed at a rate much more rapid than the rate of polymerization of Q. The latter conclusion follows from two observations: that the rate of disappearance of the absorption due to Q is independent of the amount of excess dichromate added originally, and that addition of dichromate after Q has entirely disappeared immediately restores strong absorption at 580 mμ. It was observed that solutions of chromic acid in glacial

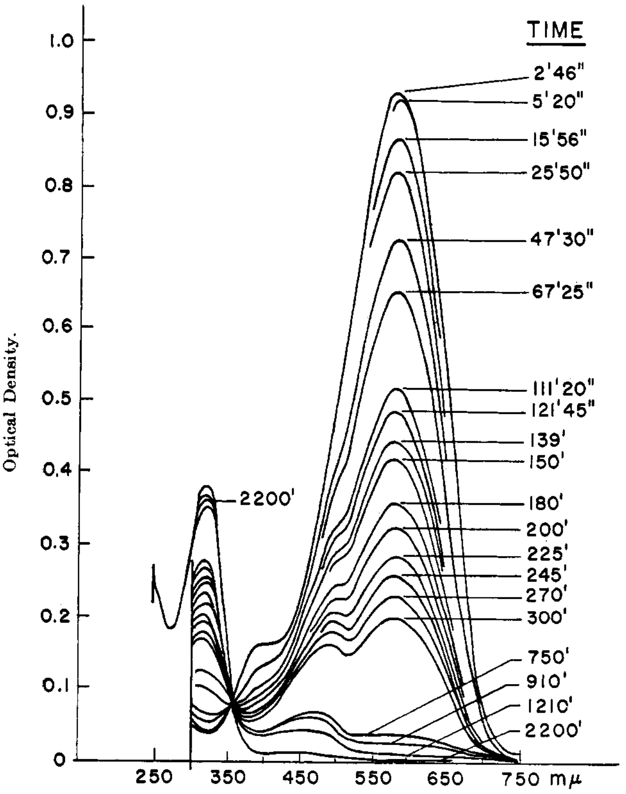

Fig. 1.—Disappearance of quinonimine in glacial acetic acid solution; $[QH_2]_0 = 2 \times 10^5$, $[K_2Cr_2O_7]_0 = 4 \times 10^5$ *N*, $[H_2SO_4] = 0.00653$ *M*, temp. = 27.8°.

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(3) L. A. Paul and L. P. Hammett, *J. Am. Chem. Soc.*, **58**, 2184 (1936); N. F. Hall and W. F. Spenseman, *ibid.*, **62**, 2487 (1940).

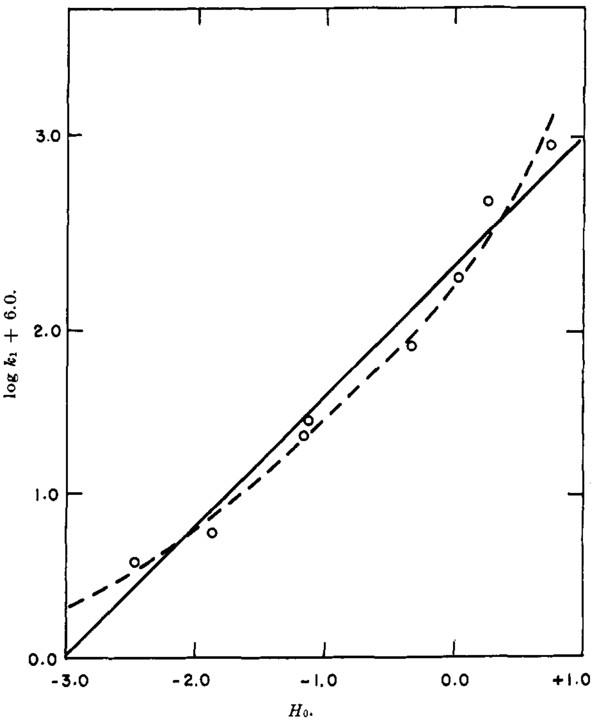
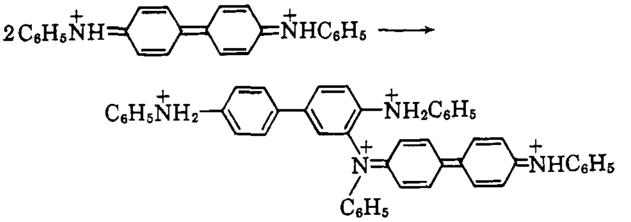


Fig. 2.—Correlation of initial rates, expressed as first-order rate constants, with H_0 for acetic acid–sulfuric acid mixtures.

acetic acid deteriorated rather rapidly. Mechanisms for catalysis of this change, which must involve oxidation of the solvent, can be readily formulated.[4]

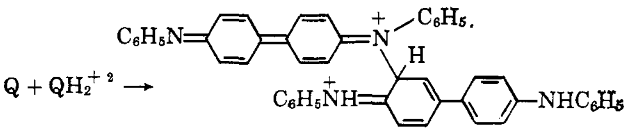
Discussion

We have referred the reaction which destroys Q as "polymerization" and have called the amorphous, greenish product a "polymer." Because of the insolubility of the product, no attempt has been made to support this view by measurement of molecular weights. The product cannot be reduced to diphenylbenzidine by zinc so that the material does not contain monomeric units held together by N–N bonds. We presume that C–C or C–N bonds are made in nuclear substitution reactions as illustrated by the following equation.



Our attempts to study the mechanism of this interesting reaction were largely frustrating. Great care was necessary to obtain reproducible experimental results and when reproducibility was obtained, the results were not easily interpretable. Clearly the reaction is inhibited by strong acid and there may be a change in mechanism (or timing) as the acidity of the reaction medium is changed. Rather interesting mechanisms, such as the one indicated below, can be devised to fit the data reasonably well but will not be discussed since the data are insufficient to lend clear-cut support to any scheme. Study of the problem has been discontinued, at least for the present, in our laboratory but we present the results as they stand because the reaction may be inherently interesting and because some of the considerable experimental difficulties involved in studying the process have been solved.

$$QH^+ \xrightarrow{\text{slow}} Q + H^+$$



Experimental

Kinetic Measurements.—Disappearance of N,N′-diphenyl-*p*,*p*′-diphenoquinonimine was followed spectrophotometrically at concentrations of 2 × 10^{-5} *M* in glacial acetic–sulfuric acid mixtures employing a Cary 14 M recording spectrophotometer. The cell compartment was thermostatted.

Materials.—Glacial acetic acid (Du Pont reagent grade) was refluxed for 24 hr. with 5 g. of chromium trioxide and 3.5 g. of acetic anhydride per liter of acid under protection from moisture. The acid was then fractionated by distillation through a 2-ft. Vigreux column at a reflux ratio of 5:1. The fraction boiling above 116.6° (uncorrected) was collected and a residue of 25% was left. The middle portion was refractionated and the material boiling above 117.0° (uncorrected) was collected and fractionally crystallized. About 30%, which had remained liquid, was discarded. The acid thus obtained had a melting point of 16.48–16.50° and was 99.94–99.95% pure.[5] The acid was stored under protection from moisture and was saturated with nitrogen, introduced through a dispersion tube, for 3–4 hr. prior to the preparation of solution. For each series of measurements a new batch of acid was prepared. Reagent grade sulfuric acid (Du Pont) was heated to boiling for 20 min. to remove reducing matter. An approximate amount of fuming sulfuric acid (30% sulfur trioxide) was added to bring the acid concentration up to about 100%. The acid was fractionally crystallized and about 20% was discarded in each operation until the melting point reached 10.3°.[6] Samples were made up fresh for each series of experiments. Stock solutions of glacial acetic acid containing known amounts of sulfuric acid were made up by weighing the latter into a volumetric flask and filling the flask to the mark with acetic acid at standard temperature. All glassware used for the preparation of solutions was flushed with nitrogen beforehand and all transfers were carried out as rapidly as possible. Potassium dichromate (Baker A.R. grade) was recrystallized once from water, dried at 110° for 6 hr., and stored in a desiccator. N,N′-Diphenylbenzidine was prepared and purified as described elsewhere.[1]

Preparation of Reagent Solutions.—A stock solution 10^{-4} *M* in N,N′-diphenylbenzidine was prepared by dissolving exactly 16.82 mg. of this substance in 500 ml. of acetic acid in a volumetric flask using the precautions mentioned previously. The solution was made up fresh for each series of measurements and used immediately after preparation. Stock solutions 2 × 10^{-4} *N* in potassium dichromate were prepared in the same way (4.895 mg. of $K_2Cr_2O_7$ per 500 ml. of acetic acid).

Both solutions were stable only if the volumetric flasks were flushed with nitrogen after each sample was withdrawn. Even with these precautions solutions could not normally be used after standing for more than 24 hr.

For kinetic runs a known amount of one of the solutions of sulfuric acid in acetic acid was pipeted into a 10-ml. volumetric flask and 2 ml. of the solution of 10^{-4} *M* diphenylbenzidine in acetic acid was added. At zero time the benzidine was oxidized by adding an appropriate amount of the potassium dichromate stock solution. After the volumetric flask had been filled to the mark with acetic acid and had been shaken well, the solution was

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[4] For example, QH_2^{+2} may equilibrate rapidly with $QH\cdot^{+2}$ and some lower oxidation state of chromium, *e.g.*, Cr^V, that can react with acetic acid.

[5] M. L. E. O. De Visser, *Rec. chim.*, **12**, 101 (1893); F. H. McDougall, *J. Am. Chem. Soc.*, **58**, 2585 (1936).

[6] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Vol. 2, part 2, 6th Ed., Springer, Heidelberg, 1951, p. 844; *cf.* R. J. Gillespie, *J. Chem. Soc.*, 1851 (1954).

poured into an optical cell and was inserted in the spectrophotometer. Thus times at which absorption bands passed through their maxima were recorded and the spectra were rescanned until the reaction had gone to 60–90% of completion. Rate constants were obtained as usual. Reverse addition of reactants did not influence reaction rates as was demonstrated in preliminary experiments.

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Mechanism of the Benzidine Rearrangement. VI.[1] Rearrangement of *p*-Hydrazotoluene

GEORGE S. HAMMOND AND JAMES S. CLOVIS[2]

Contribution No. 2902 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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As was reported by Carlin and Wich[3] the reaction of *p*-hydrazotoluene in acidic ethanol produces the *o*-semidine and disproportionation products, *p*-toluidine and *p,p'*-azotoluene. Although more than the expected amount of toluidine is formed the excess is less than previously reported. A transient oxidizing agent of unknown structure is produced. Formation of the unknown oxidant is probably associated with the high yield of toluidine. Disproportionation to amine and azo compound has been shown to be an intermolecular process by inclusion of hydrazobenzene in reaction mixtures in which hydrazotoluene is undergoing rearrangement. In such experiments very little azotoluene is produced although toluidine and the semidine are produced in the expected amounts. It is inferred that an intermediate is reduced to toluidine by reaction with either hydrazo compound.

Carlin and Wich[3] carried out an investigation of the kinetics and products of the reaction of *p*-hydrazotoluene (HzT) in ethanolic hydrogen chloride. They showed that the rate of disappearance of HzT is second order with respect to hydrogen ion and first order with respect to HzT. Three products of the reaction, *p*-toluidine, *p*-azotoluene, and 2-amino,4',5-dimethyldiphenylamine (an *o*-semidine), were reported by Carlin to account for approximately 40, 20, and 40% (by weight), respectively, of the starting material. This product distribution remained constant throughout each individual reaction and also was found to be invariant in the temperature and acidity ranges studied.

These results are typical for aromatic hydrazo compounds except for one point. Stoichiometric formation of the disproportionation products would require that equal weights (2 to 1 mole ratio) of *p*-toluidine and *p*-azotoluene be observed. However, the results indicated a 2 to 1 weight ratio of these compounds. If these data are correct, there must be a reducing agent (such as solvent) other than HzT which can be readily oxidized by the precursor of *p*-toluidine. Identification of the toluidine precursor might, by implication, lead to a better understanding of the mechanism of the benzidine rearrangement. Accordingly, a thorough investigation of the oxidizing properties of solutions of HzT in acidic ethanol and of the composition of the product mixture obtained from HzT was carried out. In conjunction with these experiments an investigation of the intermolecularity of the disproportionation reaction was conducted. The product studies were performed by employing the technique of isotope dilution. The kinetic measurements and product analyses of Carlin were repeated so that any discrepancy in results could be related to procedural rather than accidenta differences.

Experimental

***p*-Hydrazotoluene.**—Hydrazotoluene (HzT) was synthesized by the method of Carlin and Wich.[3] The crude HzT was separated from filtered zinc and zinc oxides by treatment with hot benzene. Large quantities of benzene had to be used to obtain reported yields.

***p*-Azotoluene.**—*p*-Azotoluene (AzT) was recovered from rearrangements of HzT and purified by recrystallization from ethanol, ethanol–water, and ethanol again. Sublimation at 60–70° and 1 μ sometimes was performed.

***o*-Semidine.**—This compound could be obtained most easily in a relatively pure state by the rearrangement of HzT in the presence of a limited excess of added hydrochloric acid. For example, a solution of 2.5 g. (0.0118 mole) of purified HzT, in 150 ml. of nitrogen-flushed 95% ethanol was initially treated with 0.5 ml. (0.006 mole) of concentrated hydrochloric acid. After 15–20 min. another 0.5 ml. of acid was added. The resulting solution was stirred for another 30 min., cooled with ice–water, and filtered to remove precipitated *p*-azotoluene. Fifty milliliters of water was then added to the filtrate and more *p*-azotoluene was deposited. The yellow-orange solid was separated and the resulting filtrate was neutralized with 2.5 *N* sodium hydroxide. The light orange-brown *o*-semidine which precipitated was separated and weighed 0.5 g. Purification was effected by recrystallization from ethanol–water, sublimation at 70° and 1 μ, and another recrystallization from ethanol–water. The wet product was dried under vacuum, m.p. 110°.

***p*-Toluidine.**—Practical grade *p*-toluidine was purified by four to five recrystallizations from 85–100° ligroin, m.p. 42–43°.

Bindschedler's Green.—Bindschedler's green was prepared by the method described by Dewar.[4]

Würster Blue Perchlorate.—The salt was prepared from N,N,-N',N'-tetramethyl-*p*-phenylenediamine dihydrochloride by the procedure of Michaelis and Granick.[5]

***p*-Nitrotoluene-1-C^{14}.**—Forty milligrams of toluene-1-C^{14} having an activity of 0.5 mc. was distilled under vacuum into 20 ml. of purified reagent grade toluene contained in a receiver immersed in an acetone solid. This solution was transferred with numer-

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(1) Part V: G. S. Hammond, B. Seidel, and R. E. Pincock *J. Org. Chem.*, **28**, 3275 (1963).

(2) National Institutes of Health Predoctoral Fellow, 1961-1962.

(3) R. B. Carlin and G. S. Wich, *J. Am. Chem. Soc.*, **80**, 4023 (1958).

(4) M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946).

(5) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943).