From the acetylation of 134 g. (1.25 moles) of *o*-toluidine in benzene by acetic anhydride there was obtained 135 g. of the acet-*o*-toluidide melting at 108°. Bromination in about 50-g. lots, by the procedure of Bogert and Hand,[14] gave an 80% yield of the bromo-acet-*o*-toluidide. This was nitrated by fuming nitric acid.[15] The acetyl group was removed by hydrolyzing 25-g. lots of the nitrated product with 30 cc. of concd. hydrochloric acid in 120 cc. of ethyl alcohol, and the yield was 52 g. of bromo-amine melting at 134° (all the initial 135 g. of acet-*o*-toluidide being used in the successive reactions). The amino group was then replaced by bromine in essential accordance with the procedure of Holleman,[16] to give 23 g. of 2,5-dibromo-3-nitrotoluene melting at 68–69° after crystallization from petroleum ether (b. p. 60–68°).

A mixture of 14.2 g. (0.048 mole) of 2,5-dibromo-3-nitrotoluene and 6.86 g. (0.052 mole) of potassium phenoxide was heated for three hours at 170°. The cooled reaction mixture was shaken with ether and water, and the residue obtained by evaporation of the ether was crystallized from petroleum ether (b. p. 60–68°) to give 12 g. or an 81% yield of 2-nitro-4-bromo-6-methylphenyl ether melting at 92–94°. The nitro group was reduced by dissolving 12 g. (0.039 mole) of the compound in 150 cc. of dry ether to which 20.85 g. (0.093 mole) of stannous chloride had been added, and then saturating the resulting solution with hydrogen chloride at 0°. The hydrochloride separated as a light brown solid (10.9 g.), and this was diazotized without further purification. Finally, the diazonium solution was added slowly to 150 cc. of boiling 50% sulfuric

(14) Bogert and Hand, THIS JOURNAL, **27**, 1479 (1905).

(15) Wroblewski, *Ann.*, **192**, 206 (1878). See, also, Niementowski, *Ber.*, **25**, 869 (1892).

(16) Holleman, *Rec. trav. chim.*, **27**, 155 (1908).

acid contained in a 500-cc. distilling flask which was connected to a condenser so that volatile products could be collected by steam distillation during the addition of the diazonium solution. The yield of 2-bromo-4-methyldibenzofuran was 4 g., and the compound crystallized from alcohol in the form of needles melting at 106–106.5°.

Anal. Calcd. for $C_{13}H_9OBr$: Br, 30.62. Found: Br, 30.43, 30.23.

2-Bromo-4-methyldibenzofuran was converted quantitatively to 4-methyldibenzofuran by shaking with hydrogen in the presence of palladium–calcium carbonate catalyst. The authors are grateful to Jack Swislowsky for this experiment.

The bromomethyl compound was unaffected by refluxing for four days with alkaline potassium permanganate, a mixture of potassium permanganate and dilute nitric acid at 180° for eight hours, and an alkaline solution of potassium ferrocyanide at reflux temperature for twelve hours. When treated with an acetic acid solution of chromic acid for four hours at 50°, the compound was partially destroyed but no acid could be isolated, and some unchanged compound was recovered. In the same solution at the boiling point, the compound was completely destroyed. The use of chromic acid in dilute sulfuric acid also destroyed the compound without stopping at the desired dibenzofuran-carboxylic acid.

Summary

It has been shown that bromination and nitration of methyl 4-dibenzofurancarboxylate give heteronuclear substitution products.

The Reduction of Silver Ions by Hydroquinone

BY T. H. JAMES

No detailed investigation of the mechanism of the reaction between silver ions and hydroquinone appears to have been made, although the reaction is of considerable interest in connection with the study of the mechanism of photographic development and fogging action. In the present investigation, we have studied the reaction in gelatin and in gum arabic solutions. The use of a protective colloid served both to facilitate the study of the catalytic phenomena involved and to allow a somewhat closer approach to conditions which would exist in the case of a reaction between free silver ions and hydroquinone in the development process.

Materials and Procedure

Hydroquinone and Silver Nitrate.—The Eastman Kodak Company preparations were purified further by recrystallization.

Buffer Salts.—General Chemical Company reagent grade. Both acetate and phosphate buffers were used, although the low solubility of silver phosphate limited the use of the latter to low silver nitrate concentrations.

Colloidal Silver.—Carey Lea's, dextrin reduction.

Colloidal Gold.—Red sol, phosphorus reduction, 0.0728 g. gold per liter.

The solutions were prepared in two parts, the first containing the silver nitrate and stabilizing colloid (gelatin or gum arabic) and the second containing the hydroquinone and buffer. A total solution volume of 150 ml. was employed. After the solutions had attained the temperature of the thermostat (20 $\pm$ 0.05°, unless otherwise specified) they were mixed quickly. At regular intervals, 10-ml. samples were pipetted off and rapidly added to 10 ml. of 30% sodium thiosulfate solution, which effectively stopped the reaction. The time required for emptying the pipet was two seconds. Density determinations were made by means of a photronic cell turbidimeter within two minutes after addition of the reaction mixture to the thiosulfate. No significant destruction of silver by re-

action with thiosulfate occurred within this period. All reactions were carried out under a dim red light, although control experiments failed to show significant effect of diffuse white light. Determinations of pH were made by means of a glass electrode on duplicate solutions complete except for addition of silver nitrate.

Experimental Results

A noticeable reaction between the silver nitrate and hydroquinone takes place only after a relatively long induction period. The addition to the reaction mixture of small quantities of colloidal silver, gold, palladium, or silver sulfide greatly reduces this induction period. Some decrease is also effected by quinone (see Fig. 1). The reaction is thus markedly autocatalytic, and the major portion of the catalysis is due to the silver, since further experiment showed that the addition of quinone to a reaction mixture already inoculated with colloidal silver did not measurably increase the reaction rate.
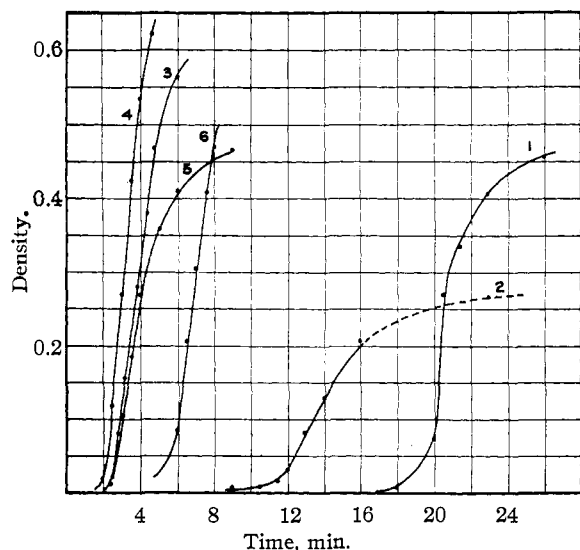

Fig. 1.—Reduction of silver nitrate by hydroquinone, 1% gelatin: 1, no addition; 2, 0.1 mmole quinone; 3, silver sol added; 4, gold sol added; 5, palladium sol added; 6, silver sulfide sol added.

In the kinetic investigation of the catalyzed reaction, 2.00 ml. of gold sol was added to the reaction mixture at the start of the experiment. Colloidal gold was used in preference to silver because of the purity of the preparation and the uniformity of particle size. Gum arabic was employed as protective colloid in most of the work. However, all major kinetic results were checked by experiments with silver sol addition and photographic gelatin (isoelectric point, 4.9) as protective colloid.

A reasonably linear relationship between density and the amount of silver was obtained in the region of interest when nucleation was by colloidal gold. This is shown in Fig. 2. When colloidal silver was employed, the amount of silver varied approximately as the 1.6 power of the density. This difference in the silver–density relationship may be attributed to the much larger particle size involved in the latter case.
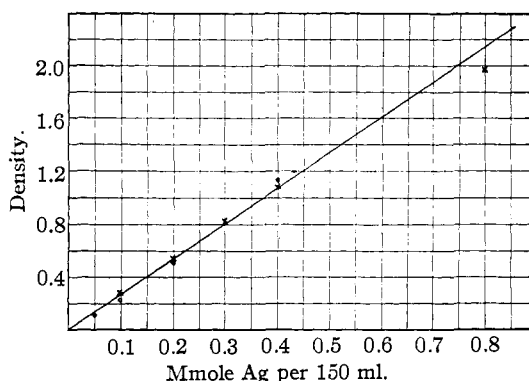

Fig. 2.—Silver–density relationship.

The initial part of the reaction curve for the gold-inoculated solution is well represented by the equation

$$dx/dt = Kx^{2/3} \qquad (1)$$

where x is the mass of reduced silver. This is indicated by the linearity of the relation between $D^{1/3}$ and time (see curve II, Fig. 3). An alternative rate equation which sometimes holds for autocatalytic reactions, $i.\ e.$

$$dx/dt = Kx \qquad (2)$$

yields a less satisfactory representation of the data. In the following, accordingly, the reaction rates are expressed in terms of the slopes of the straight-line portions of the $D^{1/3}$–t plots (time expressed in minutes).

The reaction rate is *proportional to the hydroquinone concentration*, and, under the conditions

TABLE I
VARIATION OF REACTION RATE WITH HYDROQUINONE CONCENTRATION

Gum arabic, 1 per cent.; gold sol, 2.0 ml.

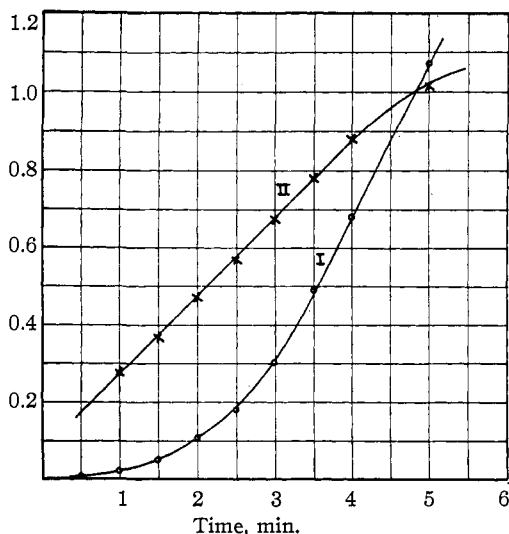| Amount of hydro-quinone. mmole	Acetate buffer. pH 5.74 AgNO₃. 0.40 mmole Rate	R/hydro-quinone	Phosphate buffer. pH 6.4 AgNO₃. 0.20 mmole Rate	R/hydro-quinone
0.25	0.035	0.140	0.09	0.36
.375			.145	.38
.50	.077	.154	.20	.40
1.00	.145	.145	.375	.375
1.50			.50	.33
2.00	.335	.167		

Fig. 3.—Curve representing catalyzed reaction: curve I, D–t plot; curve II, $D^{1/3}$–t plot; AgNO₃, 0.80 mmole; hydroquinone, 1.00 mmole; colloidal gold. 2.00 cc.

employed, the reduction goes nearly to completion so that the reverse reaction between quinone and silver is negligible.

The variation of the reaction rate with pH is given in Table II.

TABLE II

VARIATION OF REACTION RATE WITH pH

Acetate buffer, 25 ml. 0.2 M sodium acetate plus x ml. 0.1 M acetic acid; gum arabic, 1 per cent.; AgNO₃, 0.40 mmole; hydroquinone, 1.00 mmole.

pH	Rate	$D_{max.}$	Rate calcd. for monovalent ion
6.27	0.41	1.07	0.38
6.06	.275	1.06	.245
5.74	.145	1.07	.115
5.45	.088	1.07	.058
5.15	.060		.030

A plot of log R against pH gives a somewhat curved line which approaches a slope of 1.0 as the pH increases. The data are well represented by the equation

$$\text{Rate} = K'[C_6H_5O_2^-] + K''[C_6H_6O_2] \quad (3)$$

If 0.03, the rate of reaction between the un-ionized hydroquinone and the silver ions, is subtracted from the measured rates given in Table II, a plot of the logarithm of the resultant rates against pH yields a straight line of slope 1.0 (broken curve, Fig. 4).

The reaction rate does not increase proportionately with the *silver-ion concentration*, but follows instead an expression of the form of the Freundlich isotherm with an exponent of about
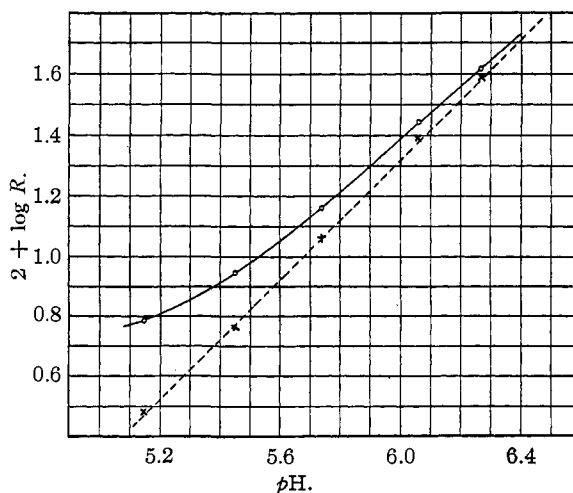

Fig. 4.—Dependency of rate upon pH: —O——O—, measured rate; -x---x-, rate corrected for reaction of un-ionized hydroquinone.

$^2/_3$. This is indicated by the data in Table III and the log–log plot in Fig. 5.

TABLE III

VARIATION OF RATE WITH SILVER-ION CONCENTRATION

Acetate buffer, pH 5.74; gum arabic, 1 per cent.; hydroquinone 1.00 mmole.

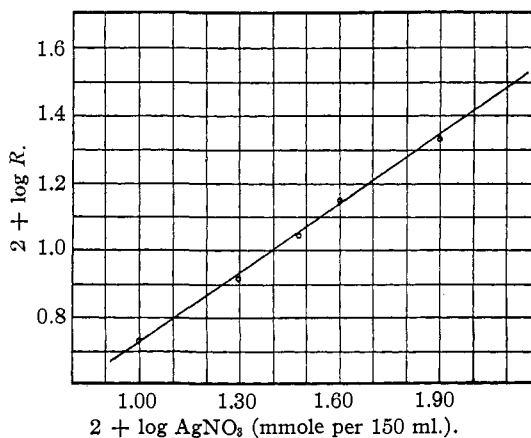| AgNO₃. mmole	Rate
0.10	0.054
.20	.081
.30	.110
.40	.142
.80	.212

Fig. 5.—Variation of rate with [Ag⁺].

The reaction rate is approximately inversely proportional to the *concentration of gum arabic*.

The temperature coefficient of the reaction is approximately 2.1. This would indicate an activation energy of around 12,700 cal. However, if the univalent ion is the active species, correction must be made for heat of dissociation. The avail-

TABLE IV

VARIATION OF RATE WITH GUM ARABIC CONCENTRATION

% gum arabic	Phosphate buffer. pH 6.4 AgNO₃, 0.20 mmole hydroquinone 0.50 mmole	Acetate buffer. pH 5.74 AgNO₃, 0.40 mmole hydroquinone 1.00 mmole
0.50	0.38	0.27
1.00	.20	.145
2.00	.093	.066

able data on the temperature dependence of the primary ionization of hydroquinone indicate for this the rather large value of 6900 cal.[1] The apparent activation energy would thus be reduced to about 5800 cal. Heats of adsorption may enter to alter this figure.

TABLE V

VARIATION OF RATE WITH TEMPERATURE

Gum arabic, 1 per cent.; AgNO₃, 0.40 mmole; hydroquinone, 1.00 mmole; acetate buffer.

Temp., °C.	Rate		pH	Log 100 R (corrected for change in pH)
14.5	0.111			
15	.118		5.82	1.00
20	.145	0.143	5.74	1.16
25	.180	.178	5.66	1.32

Discussion

At the start of the reaction catalyzed by the addition of colloidal gold, the gold particles quickly will become covered with silver, so that the measured kinetics are in reality those of the silver-catalyzed reaction. As the reaction progresses, the average particle size increases steadily. The formation of new particles during the reaction does not appear probable from the results of experiments in which no nuclei were added to the reaction mixture. Equation (1), which adequately represents the early portion of the reaction, may be derived readily upon the assumption that we have to deal with a fixed number of spherical particles and that the reaction rate is proportional to the silver surface.

The dependence of the reaction rate upon the ²/₃ power of the silver-ion concentration indicates that the silver ions react only after adsorption to the catalyst. This relation could hardly be understood if the catalyst served merely as deposition centers for silver present in a supersaturated solution. On the other hand, no adsorption of hydroquinone is indicated, although the assumption that weak adsorption occurs would not be incompatible with the experimental results.

The dependence of the reaction rate upon the solution pH indicates that both un-ionized hydroquinone and the univalent hydroquinonate ion are active in the pH range studied, although the specific rate of reaction of the univalent ion should be about 5×10^4 greater than that of the un-ionized hydroquinone.

No effect upon the reaction rate could be detected when quinone, up to 0.25 mmole, was added to a reaction mixture inoculated with colloidal silver or gold. Hence, quinone catalysis does not play a significant part in the silver-catalyzed reaction. The observed decrease in the induction period in the absence of added colloidal gold or silver indicates that a quinone catalysis of the primary homogeneous reaction between silver ions and hydroquinone does occur. The mechanism of this catalysis may be the same as that postulated by James and Weissberger[2] for the autoxidation of durohydroquinone and ψ-cumohydroquinone, i. e., a primary reaction of the quinone with the divalent hydroquinonate ion to form a very active semiquinone. A similar reaction between quinone and the univalent ion or un-ionized hydroquinone would not be expected to occur.

The indicated mechanism of the reduction of silver ions by hydroquinone is in contrast to that which Roberts and Soper[3] assume for the reduction of silver ions by ferrous ions. Their results indicate that the homogeneous reaction between ferrous ion and silver ion is very rapid in comparison with the rate of deposition of silver on condensation nuclei, the latter being in this case the rate-controlling process. In contrast to the results which Roberts and Soper obtained with the ferrous ion–silver ion reaction, it is observed that an increase in ionic strength of the hydroquinone–silver ion catalyst reaction mixture is accompanied by a decrease in reaction rate—a result in accord with expectations for the salt effect upon a reaction between oppositely charged ions, but not in accord with expectations for the salt effect upon the rate of deposition of silver from a supersaturated solution. It is not surprising, however, that the rate of homogeneous reaction between hydroquinone and silver ion is much slower than that of the ferrous ion–silver ion reaction, since the former process involves an unequal transfer of electrons between the two reaction particles.[4]

(1) S. E. Sheppard. Trans. Am. Electrochem. Soc., 39, 440 (1921); H. von Euler and E. Brunius. Z. physik. Chem., 139, 615 (1928); A. E. Cameron, J. Phys. Chem., 42, 1217 (1938).

(2) T. H. James and A. Weissberger. THIS JOURNAL, 60, 98, 2084 (1938).

(3) D. Roberts and F. G. Soper. J. Chem. Soc., 2004 (1932).

(4) Cf. P. A. Schaffer. J. Phys. Chem., 40, 1021 (1936).

Summary

1.   The reaction between silver ion and hydroquinone in slightly acid solution is strongly catalyzed by colloidal silver, gold, palladium and silver sulfide.

2.   The rate of the reaction catalyzed by silver varies as the first power of the hydroquinone concentration and as the $2/3$ power of the silver-ion concentration.   The dependence of the rate upon the hydroxyl-ion concentration indicates that both un-ionized hydroquinone and the univalent ion take part in the reaction in the pH range 5.15–6.27.

3.   The rate of the catalyzed reaction varies proportionately with the surface of the catalyst, and inversely with the concentration of gum arabic present as stabilizer.   The temperature coefficient at pH 5.74 is approximately 2.1.

4.   The indicated mechanism involves primary adsorption of silver ions to the surface of the catalyst.

[Contribution from the Department of Chemistry of Duke University]

Saturated Standard Cells with Small Temperature Coefficients. III. Cadmium–Bismuth Amalgams of Constant Cadmium Activity

By W. C. Vosburgh and Helen C. Parks

A modified Weston standard cell has been described[1] that has a temperature coefficient less than a third that of the Weston cell and seems to be as satisfactory otherwise as the Weston cell. One respect in which this cell is different from the Weston cell is in the use of a cadmium–bismuth amalgam instead of the cadmium amalgam. Vosburgh[2] made a brief preliminary study of cadmium–bismuth amalgams, and it is the purpose of this paper to report an investigation of the composition limits within which such amalgams have a constant cadmium activity.
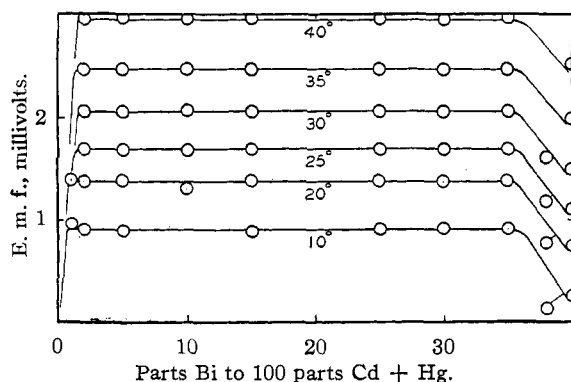

Fig. 1.—Electromotive force of the cell $Cd(Bi,Hg)/Cd^{++}/Cd(Hg)$ when the proportion of bismuth in the ternary amalgam varies and the ratio of cadmium to mercury is fixed at 13:87 parts by weight.

(1)   Paper II.   Vosburgh, Guagenty and Clayton.   This Journal, **59**, 1256 (1937).
(2)   Vosburgh, *ibid.*, **47**, 2531 (1925); see also ref. 1.

Amalgam concentration cells were made in which one amalgam was a two-phase cadmium amalgam containing about 10% cadmium and the other a cadmium–bismuth amalgam. The compositions by weight of the various ternary
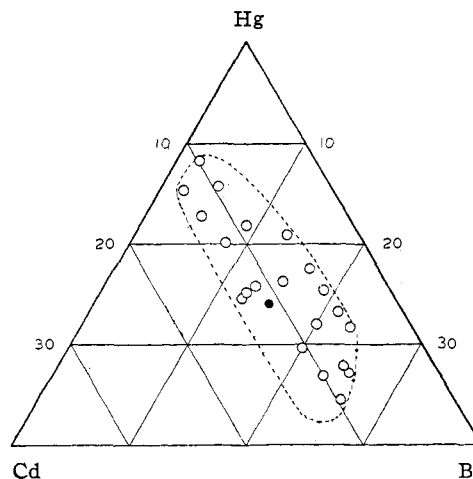

Fig. 2.—Cadmium–bismuth amalgams of constant cadmium activity at 25°. The dotted line is the approximate boundary of the region of constant cadmium activity. Circles represent experimental points; ●, represents the composition 11% Cd, 15% Bi and 74% Hg.

amalgams used are given in Table I. The electrolyte was saturated cadmium sulfate solution, with an excess of cadmium sulfate crystals at each electrode.