

Electrochemical Studies on the "Hydrazine Effect"

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Abstract

The mechanism for the hydrazine effect has been proposed by Simson as the successive processes started with the oxidation of N'-Acyl-N-phenylhydrazines(AH) by p-benzoquinone(Q) in PQ-developers to produce N'-Acyl-N-phenyldiazenes(AD). AD is hydrolyzed to produce a strong reducing substance phenyldiazenes(D) which makes unexposed silver halides developable by its fogging action. Today this mechanism is generally recognized, but any evidences in support of the formation of D have not yet obtained. Recently Kawato et al. reported that D possesses a absorbance maximum at 350 nm. The results obtained using electrochemical methods as well as spectrochemical methods in the present paper were consistent with the Kawato's report. However any anodic wave for the electrooxidation of D were not observed even in the solution of which spectra showed a maximum at 350 nm. The formation of AH in alkaline solution of AD, which was confirmed by the measurement of the current-potential curve of the solution, was a unique evidence in support of the formation of a very strong reducing substance through hydrolysis of AD.

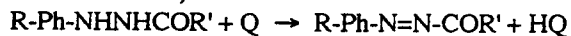
Introduction

The mechanism for infectious development caused by addition of N'-acyl-N-phenylhydrazines(R-Ph-NHNH-COR') to a developer including hydroquinone(HQ) has been proposed as the following successive processes.¹

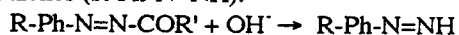
(1) Silver halides with latent image(AgX(Ag^o)) are developed by HQ.



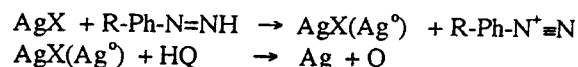
(2) The oxidation product p-benzoquinone(Q) oxidizes R-Ph-NHNH-COR' to form N'-acyl-N-phenyldiazenes (R-Ph-N=N-COR').



(3) R-Ph-N=N-COR' are hydrolyzed to form N-phenyldiazenes (R-Ph-N=NH).



(4) R-Ph-N=NH makes the unexposed silver halide(AgX) developable by the fogging action.



Some studies supporting this mechanism have been reported. Kitchin et al.² titrated N-phenyl-N'-formylhydrazine with silver nitrate and found that 1 mole of the hydrazine requires 2.8 moles of silver ion for complete oxidation. Shinohara et al.³ reported a kinetic study in which they concluded that removal of N'-acyl group from N'-acyl-N-phenyldiazene by the hydrolysis(step 3) is the rate limiting process. Kawato et al.⁴ oxidized N-(4-phenylsulfonamidophenyl)-N'-formylhydrazine with MnO₂ in CH₃CN including triethylamine and then hydrolyzed by addition of H₂O to produce D. By analyzing rate constants of electron transfer reaction from D to several compounds with various reduction potentials according to Marcus theory, they obtained -0.36 V vs. Ag/AgCl as the oxidation potential of D. They observed the optical absorbance spectrum of AD (λ_p : undissociated=350nm, dissociated=480nm) and D (λ_p : undissociated=280nm, dissociated=350nm).

Encouraged by the Kawato's report, in the present paper we investigated the following reactions of the AH oxidation in alkaline H₂O/CH₃CN solution or in CH₃CN, using electrochemical methods, spectrochemical methods, or combined methods of the two methods, and attempted to obtain some pieces of evidence in support of the formation of D.

Experimental

N'-Acyl-N-phenylhydrazines The structures of acylhydrazines and an acyldiazene used here are shown in Fig.1. These compounds were provided by Fuji Photo Film Co..

Solutions. The electrolyte were H₂O/CH₃CN mixture including 0.05 M H₃BO₃(pH9~10) or Na₂CO₃(pH10~12) and 0.10 M NaClO₄, or CH₃CN including 0.1 M tetrabutylammonium bromide hydrochloride and 0.01 M triethylamine hydrochloride. The pH was adjusted by adding NaOH or H₂SO₄. The chemicals were of reagent grade and used without further purification.

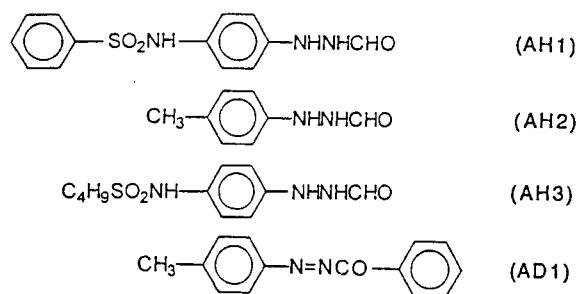


Figure 1. Structures of the used *N*'-formyl-*N*-phenylhydrazines and *N*'-benzoyl-*N*-tolylidiazene.

Electrochemical experiments. As working electrode, a rotating Au disc electrode and a gold mesh electrode were employed for the rotating electrode method and for the spectroelectrochemical method, respectively. The reference electrodes were a saturated saturated Ag/AgCl electrode in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ or a silver-wire in CH_3CN electrolyte. The counter electrode was a Pt-wire which was placed in a compartment separated from the working electrode compartment by sintered-glass. The rotating electrode with speed-controller and the dual potentiostat, and the function generator with potentiostat were HR-102, HR-101B, and HAB-151(Hokuto Denko Co., Ltd.), respectively. The spectroelectrochemical cell is shown in Fig.2. It was placed in a double beam spectrophotometer(Shimadzu Co. Ltd., UV-180). The measurements were carried out at 25°C under Ar gas.

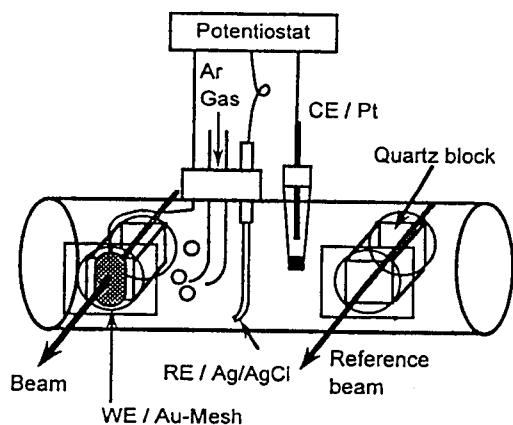


Figure 2. Schematic diagram of the for spectroelectrochemical measurements.

Activation of working electrodes. The disc was first polished by diamond paste($1\mu\text{m}$), the mesh was first washed in hot water, followed by washing in hot sulfuric acid solution. Then they were activated in the supporting electrolyte with cyclic linear sweeps(2 V s^{-1} ; 50 cycles) in the potential range between -2 and 2 V . The working electrode was strongly

inhibited by electrode reaction products adsorbed at the electrode surface, and application of a very high negative potential(-2 V) for 1 s every second was required also during the measurement of a voltammogram at the disc.

Spectrochemical experiments. The spectra were recorded on the Shimadzu double beam Spectrophotometer UV-180. Measurements were carried out in the air.

Results and Discussion

Figure 3 shows change of spectra of an equimolar CH_3CN solution of AH1 and Q including dimethylamine. Without alkali the redox reaction between the two compounds did not proceed. The progress of the reaction was monitored by measurement of the same solution. The wave of Q was completely replaced by a more negative cathodic wave which could be attributed to the reduction of AD(Fig.4). Two peaks appeared at 350 nm and 480 nm and they increased with time. The Former and the latter are due to undissociated AD and dissociated AD, respectively⁴. Immediately after addition of the aqueous alkaline buffer the peak of undissociated AD disappeared, as shown in Fig.5. The peak of dissociated AD decreased slowly in height, and another peak at 350 nm appeared, which is due to D^4 . In change in height of the two peaks an isosbestic point was observed. The results suggest that D is produced directly through hydrolysis of AD and that D is not oxidized by AD. With MnO_2 as the oxidizing agent, the oxidation of AH did not proceed even in large excess with MnO_2 .

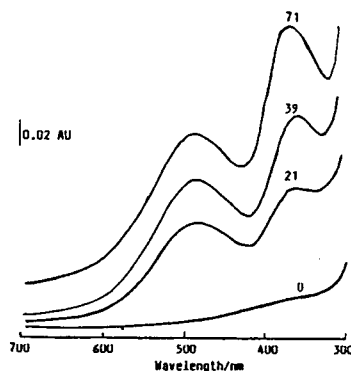


Figure 3. Change of spectra of equimolar CH_3CN solution of AH1 and Q in cluding dimethylamine with time(min) after mixing.

The spectra of AH1/Q mixture in $\text{H}_2\text{O}/\text{CH}_3\text{CN}(1/2)$ solution of $\text{pH}9.5$ are shown in Fig.6($C_Q/C_{\text{AH1}}=1$) and Fig.7($C_Q/C_{\text{AH1}}=1.5$). In the equimolar solution of AH1 and Q two peaks at 350 and 480 nm were observed, whereas in excess with Q only the peak at 480 nm was observed. This suggests that D is oxidized by Q. This is also confirmed by the following electrochemical measurement.⁵ Fig. 8 shows a potential-current curve of AH1/Q mixture ($\text{H}_2\text{O}/\text{CH}_3\text{CN} =$

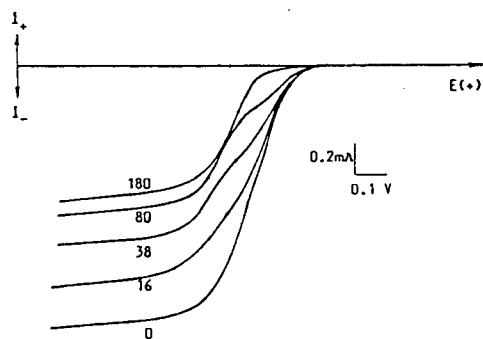


Figure 4. Change of Current-potential curves with time(min), measured simultaneously with Fig.3.

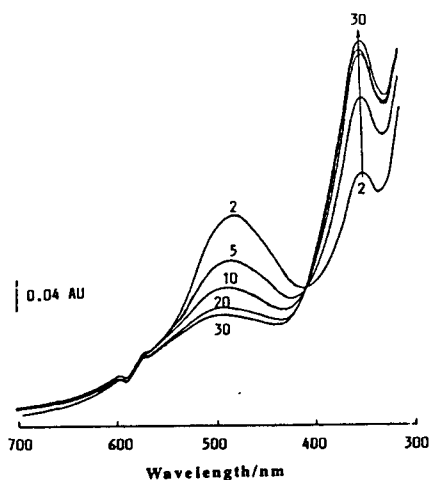


Figure 5. Change of spectra with time(min) after the addition of aqueous buffer to the solution of Fig.3(oxidation time=71 min). $H_2O/CH_3CN=1/1$, pH10.

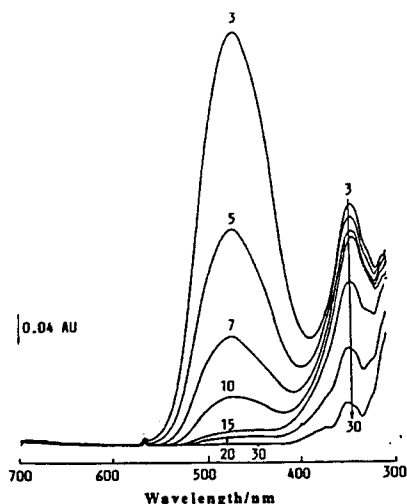


Figure 6. Change of spectra of equimolar $H_2O/CH_3CN(1/2)$ solution of AH1 and Q of pH9.5 with time(min) after mixing.

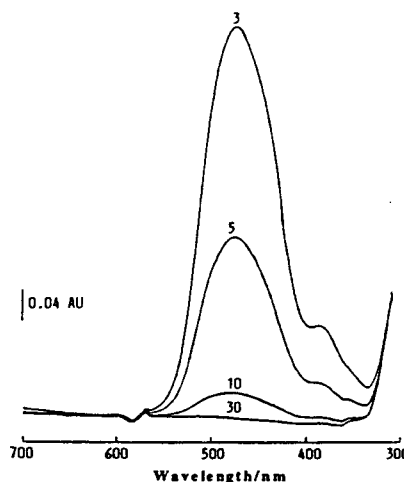


Figure 7. Change of spectra of $H_2O/CH_3CN(1/2)$ solution of AH1 and excess Q($C_Q/C_{AH}=1.5$) of pH9.5 with time(min) after mixing⁵.

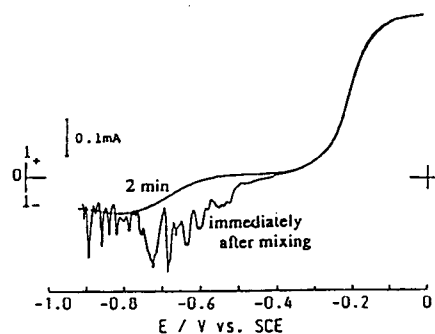


Figure 8. Change of the cathodic current-potential curves of the AH2(5.0×10^{-4} M)/Q(4.0×10^{-4} M) mixture solution ($H_2O/CH_3CN=1/1$, pH11.5) with time after mixing⁵.

1/1, pH11.5). The cathodic wave observed immediately after the Q addition was replaced in several decades of seconds by a more negative cathodic wave. The height of this wave increased linearly and then tended to a constant value. The Q concentration at the turning point corresponded to the concentration ratio $C_Q/C_{AH}=1.5$. This observation is compatible with $C_{AgNO_3}/C_{AH}=2.8$, which is reported by Kitchin et al.³ for the complete oxidation of AH by $AgNO_3$.

The result supporting the production of D by electrooxidation was obtained by the spectroelectrochemical measurement. Fig.9 shows a cyclic voltamogram of AH2 in $H_2O/CH_3CN(1/1)$, pH11.5) and the simultaneously measured optical response at several wavelengths. The anodic peak is for the oxidation of AH2 to AD. The absorbance obtained with the oxidation of AH2 increased and then decreased in the wavelength region from 440 to 520 nm. This corresponds to formation and hydrolysis of AD. On the other hand, the absorbance observed in the region from 330 to 400 nm increased and then remained constant. This absorbance is attributed to formation of D.

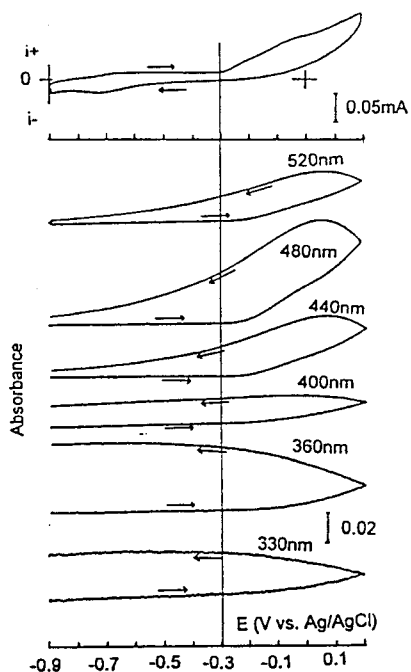


Figure 9. Current-potential and absorbance-potential curves of AH₃ (7.1×10^{-4} M) measured by the spectroelectrochemical method. $\text{H}_2\text{O}/\text{CH}_3\text{CN}=1/1$, pH11.5.

If we recognize that D is responsible for the absorbance maximum at 350 nm, the observations are excellently explained so far. But any pieces of evidence in support of D as a very strong reducing substance were not obtained. The oxidation potential -0.36 V evaluated for D by Kawato is by no means very negative, even compared with that for AH itself. The potential for electrooxidation of AH is dependent on electrode materials. Fig.10 shows cyclic voltammograms of AH₃ on a stationary Au electrode. A prepeak with the oxidation potential about -0.5 V was observed. This is due to strong adsorption of the product of the electrode reaction, here AD. On Pt electrodes this prepeak was not observed.

It was expected to observe an anodic wave for the electrooxidation of D. But any anodic wave to be regarded as the electrooxidation of D was not observed even in the solution of which spectra shows the maximum at 350 nm.

In the current-potential curve measured in alkaline $\text{H}_2\text{O}/\text{CH}_3\text{CN}(1/1, \text{pH}11.5)$ solution of AD1 (Fig.11) the production of AH was observed⁷. The cathodic first and the second wave are corresponding to those shown in Fig.8. The anodic wave is for the AH oxidation. This suggests the reduction of the AD by a more stronger reducing substance than AH, and this substance can be regarded as D. I suppose that this observation is an almost unique evidence in support of a strong reducing substance through hydrolysis of AD.

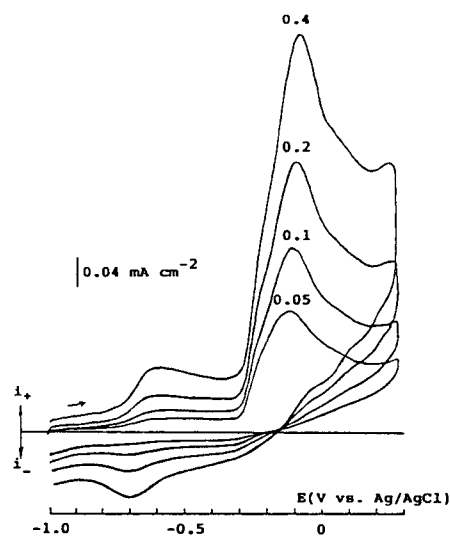


Figure 10. Cyclic Voltammograms of AH₂ (5.0×10^{-4} M) in $\text{H}_2\text{O}/\text{CH}_3\text{CN}(1/1, \text{pH}11.2)$ solution. Parameter: Sweep rate (V s^{-1}).

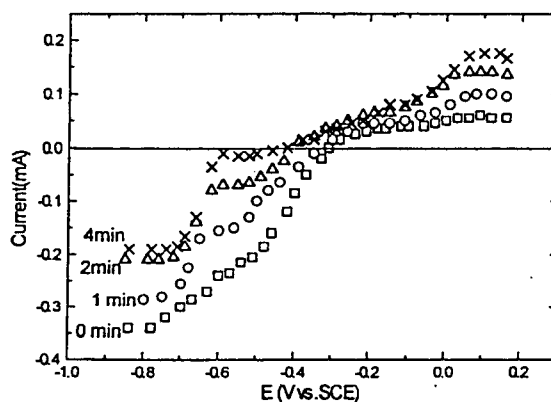


Figure 11. Change of the cathodic current-potential curves of AD1 (4.6×10^{-4} M) in with time after its addition to the $\text{H}_2\text{O}/\text{CH}_3\text{CN}(1/1, \text{pH}11.7)$ solution⁷.

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