

## The kinetics of disulfide bond reduction in hair by ammonium thioglycolate and dithiodiglycolic acid

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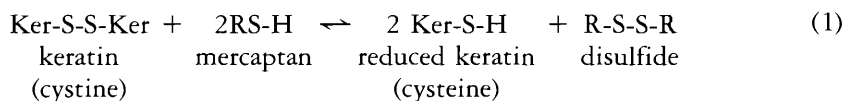
### Synopsis

A study was conducted to determine the physical behavior of human hair in the presence of ammonium thioglycolate (ATG) and the effect of dithiodiglycolic acid (DTDG) on this behavior. The method utilized in this study was a modification of the single fiber tensile kinetics (SFTK) method (1). SFTK experiments were performed using the miniature tensile tester (Dia-stron) on virgin hair from a single source (DeMeo Brothers) by monitoring stress-relaxation and stress/strain behavior (20% index). The results indicate that the addition of dithiodiglycolic acid does not affect the kinetics of stress relaxation when the fiber is held under a constant strain (1.5%). Similarly, the addition of dithiodiglycolic acid does not diminish the extent of fiber weakening prior to neutralization. However, hair reduced in the presence of dithiodiglycolic acid is stronger after neutralization than hair reduced in the absence of dithiodiglycolic acid.

### INTRODUCTION

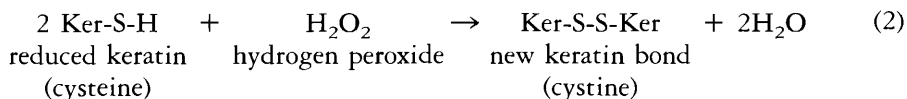
Numerous studies have been undertaken to determine the effects, both physical and chemical, that reducing agents have upon the hair. It has been well established that the mercaptans used to produce a permanent wave attack the disulfide bonds in the hair, cleaving these bonds so that they may later be reformed in a new configuration. Previous studies have investigated the kinetic behavior and mechanisms of action of various mercaptans by monitoring the stress-relaxation and stress/strain behavior of hair or wool fibers (1–11). The findings of these studies indicate the dramatic effects that may result when parameters such as temperature, pH, or concentration are varied.

The overall reactions involved in the waving of hair (Eqs. 1 and 2) are:



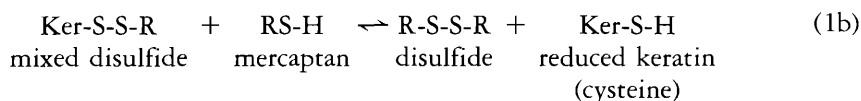
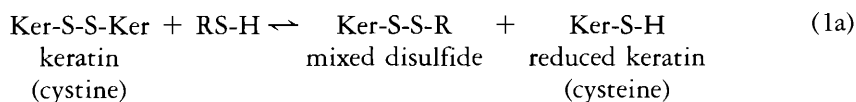
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Although other oxidizing agents, including atmospheric oxygen, have been utilized, hydrogen peroxide (Eq. 2) is the most commonly used oxidizing agent to date.

The overall reaction (Eq. 1) proceeds through two steps. Each of these steps is a displacement reaction by the mercaptan ion,  $\text{RS}^-$ , on a sulfur atom of the disulfide bond, then by the mercaptan ion on a sulfur atom of the mixed disulfide (12). The two displacement reactions (Eqs. 1a and 1b) are:



The overall equilibrium constant,  $K_a$ , of the above reactions (Eqs. 1a and 1b) is expressed as:

$$K_a = \frac{[\text{R-S-S-R}] * [\text{Ker-SH}]^2}{[\text{Ker-S-S-Ker}] * [\text{R-SH}]^2} \quad (3)$$

The equilibrium positions and extent of the reactions given by Equations 1 and 2 are governed by pH, concentration, tension applied during rolling, nature of mercaptan employed, degree of fiber swelling, time, and temperature (12,13).

Much research has been performed to describe the kinetics and mechanisms by which reducing agents function (1-11). Currently, there are two mechanisms cited in the literature: pseudo first-order kinetics and moving boundary kinetics. Pseudo first-order kinetics are exhibited by sodium thioglycolate (TGA) below pH 9 (1) and bisulfite (4). The assumptions made in applying this kinetic model are: 1) the diffusion of the reducing agent into the hair fiber occurs rapidly, 2) the reducing agent is present in large excess and remains constant during the reaction, and 3) the rate of disulfide reduction proceeds slowly and is the rate-determining step. The rate of disulfide bond cleavage is described by Equation 4:

$$- \frac{d(\text{S-S})}{dt} = k C_0(\text{S-S}) \quad (4)$$

where  $k$  is the reaction rate constant,  $C_0$  is the concentration of the reducing agent, and (S-S) is the number of disulfide bonds remaining at any given time (1,4). This equation is then integrated to arrive at Reese and Eyring's relationship for describing the tensile stress (Eq. 5) (4):

$$F_t = F_0 \exp^{-kC_0t} \quad (5)$$

where  $F_t$  is the force at any given time,  $F_0$  is the force before applying the reducing

agent,  $C_0$  is the concentration of the reducing agent,  $k$  is the rate constant, and  $t$  is the time (1,4).

There are two further assumptions made when applying the pseudo first-order kinetic model to chemical stress-relaxation studies of hair. The first assumption is that the tensile stress is proportional to the number of disulfide bonds remaining at any given time. The second is that all the stress-supporting bonds are equally reactive or totally nonreactive. A plot of  $-\ln(F_t/F_0)$  versus time,  $t$ , yields the rate constant,  $k$ . If the reaction is truly pseudo first-order, then a plot of the  $\ln[(F_t - F_p)/(F_0 - F_p)]$  versus time will be linear with a slope of  $kC_0$  and an intercept of zero (1,2). The rate constant,  $k$ , should remain constant regardless of the concentration of the reducing agent.

Single fiber tensile kinetics (SFTK) is a method for investigating reduction kinetics of hair using single fibers based on stress relaxation caused by disulfide bond cleavage. This method is useful for basic studies of interaction of thiols with hair (1). The data obtained from SFTK measurements are used to elucidate information about the rates and mechanisms of reactions of reducing agents and to derive mathematical models (1). Wickett used SFTK in conjunction with strain cycling to study the effects of changing pH, temperature, and concentration on reduction of individual hairs using sodium thioglycolate, dithiothreitol, and sodium dihydrolipoate solutions (1). Wickett and Barman used SFTK to study the efficacy of perms affected by the reaction with disulfide bonds and the ease of penetration using solutions of dihydrolipoic acid, dithiothreitol, 1,3-dithiopropanol and its derivatives, and 1,4-dithio-2-butanol and its derivatives (2).

For the purposes of this study utilizing the miniature tensile tester, the SFTK method was modified in order to study the effects of reduction by ammonium thioglycolate (ATG) at different pHs and the effects produced by the addition of dithiodiglycolic acid (DTDG) to an ATG solution. If the reducing agent in Equation 1a is ATG ( $\text{HS-CH}_2\text{-COOH}$ ), then the disulfide in Equation 1b is DTDG ( $\text{HOOC-CH}_2\text{-S-S-CH}_2\text{-COOH}$ ). The data obtained from stress-relaxation and stress/strain measurements were used to determine the reaction rate constants ( $k$ ) and mechanisms of reduction. SFTK results from stress/strain measurements (20% index) showing the effects of reoxidation of hair after treatment with an ATG/DTDG solution are also discussed.

## MATERIALS AND EQUIPMENT

Medium-brown, virgin hair from a single source was obtained from DeMeo Brothers, New York. This hair sample was used for all the studies described in this report. The hair fibers were shampooed with a 10% (w/w) solution of sodium lauryl sulfate in Millipore water, rinsed thoroughly, and allowed to dry.

Stress-relaxation and stress/strain measurements were made on the miniature tensile tester (Dia-stron) interfaced to an IBM 386 personal computer that ran the Rheopoc software. Temperature was controlled by a Techne® Model 1252-00 circulating water-bath. Reducing agents were obtained from Evans Chemetics, Waterloo, NJ. The reducing solutions used in this study contained only the mercaptan, Millipore water, and ammonium hydroxide to adjust pH. The neutralizer contained hydrogen peroxide, Millipore water, and phosphoric acid to adjust pH.

## METHODOLOGY

### FIBER SELECTION TEST

Hair fibers were preselected by straining the untreated fibers into the yield region in water (<25% extension) and measuring the force necessary to extend the fiber. After the untreated hair was measured, it was allowed to re-equilibrate overnight in water to recover its tensile properties. Each 30-mm fiber segment was allowed to soak in water for 60 minutes. The fiber was extended 20% in water and held for five seconds. Only those fibers exhibiting a linear Hookean region and an acceptable yield region (turnover of 2–5% and slope equal to approximately 0.1 times the slope in the Hookean region) were used for SFTK measurements.

### STRESS RELAXATION

When a hair fiber is extended in water by less than 2% of its original length, stress relaxation is complete in approximately 30 minutes (1). The utilization of a strain cycling procedure will reduce the amount of time necessary for stress relaxation. The following modification of the SFTK method was used with the miniature tensile tester to stress relax the hair fibers. The fiber was extended to 2.0% strain in a buffer solution the same pH and temperature as the reducing solution. Following extension, the hair fiber was allowed to stress relax for 60 seconds. The amount of strain was then reduced to 1.50% and the fiber was allowed to stress relax until a constant level of stress was achieved (2–3 minutes). After stress relaxation, the buffer solution was replaced rapidly by the reducing solution. SFTK data were collected to monitor the stress relaxation of the disulfide bonds in the hair fiber caused by the reducing agent. The data were displayed graphically as grams of force *versus* time by the Rheopc software (Dia-stron). Plots of the natural logarithm of  $[(F_t - F_p)/(F_0 - F_p)]$  *versus* time were prepared, and the reaction rate constant ( $k$ ) was calculated from the slope.

It is known that as hair is reduced, its swelling in water increases. Therefore, it would seem possible that some portion of measured decrease in force could be attributed to increased zero strain length of the hair due to swelling. Wortman and Souren (14) have shown that length setting does not occur; therefore, changes in length from swelling are unlikely. This result indicates that the measured decreases in force can be attributed solely to decreased fiber strength.

### REDUCTION METHOD

Two types of solutions were prepared for the following studies: ammonium thioglycolate and ammonium thioglycolate + dithiodiglycolic acid. The first type of solution contained 1M ATG in Millipore water adjusted to either pH 8.0, 9.0, or 9.5 with ammonium hydroxide. The second type of solution was prepared by combining the appropriate volumes of a 2 M ATG solution at pH 9.0 with a 1 M DTDG solution at pH 9.0 and readjusting the pH to 9.0 in order to acquire the desired solution combinations. Each 30-mm hair fiber was prestretched in a phosphate buffer of the appropriate pH and reduced in 50 ml of reducing solution. Stress-relaxation data were collected for 30 minutes during reduction.

## RESULTS

## THE EFFECT OF pH VARIATION ON REACTION RATE CONSTANT OF HAIR REDUCED BY ATG

The relationship between tensile strength and the number of disulfide bonds in the hair fiber can be used to study the effects of pH variation on the reaction rate constants and kinetics (1–11). Since it has been established that the Hookean region of the stress/strain diagram is sensitive to the degree of hydrogen bonding in the fiber, a pre-stretch in water or a buffer solution to a constant level of force would effectively break the hydrogen bonding network in the hair. Once this network has been removed, the assumption that the tensile strength of the fiber is proportional to the number of disulfide bonds remaining may be made (1–4). By monitoring the stress relaxation of the fiber in response to cleavage of disulfide bonds, the reaction rate constant and kinetic behavior may be determined. With this relationship in mind, the effects of reduction by 1 M ATG solutions at pH 8.0, 9.0, and 9.5 at 23°C were studied by collecting stress-relaxation data.

Graphs of the  $\ln[(F_t - F_p)/(F_0 - F_p)]$  versus time indicated that reduction by a 1 M ATG solution at pH 8.0, 9.0, and 9.5 at 23°C exhibits pseudo first-order kinetics. The reaction rate constant,  $k$ , for each condition was determined from the slopes of plots of  $\ln[(F_t - F_p)/(F_0 - F_p)]$  versus time, and the mean value was calculated. The results of the evaluation of the effects of reduction by 1 M ATG solutions at various pH levels on the reaction rate constants are indicated in Table I. From analysis of the results, the trend of increasing rate of reaction as the pH of the solution increases is apparent. This pH trend for ATG was similar to the results reported by Wickett (1–3) for sodium thioglycolate at pHs below 10.

## THE EFFECT OF DITHIODIGLYCOLIC ACID ON REACTION RATE CONSTANT OF HAIR REDUCED BY ATG

The effect of addition of increasing amounts of dithiodiglycolic acid to 1 M ATG solutions at pH 9.0 at 23°C on the rate of reaction was investigated by monitoring stress-relaxation behavior. Table II contains the results of stress-relaxation measurements of three different treatments performed on 30-mm hair fiber segments. From analysis of the data using the paired t-test, the effect of DTDG on the reaction rate constant was not significant when the fiber was reduced under 1.5% constant strain. Graphs of the  $\ln[(F_t - F_p)/(F_0 - F_p)]$  versus time indicated that pseudo first-order kinetic behavior of 1 M ATG, pH 9.0, 23°C, was unchanged by addition of dithiodiglycolic acid.

Table I

Reaction Rate Constants for Hair Fibers Reduced With 1 M Ammonium Thioglycolate at pH 8.0, 9.0, or 9.5 at 23°C

Treatment (pH)	$k \cdot 10^3 \text{ (s}^{-1}\text{)}$ (Mean, SD)
8.0	1.52, 0.35
9.0	4.57, 1.59
9.5	6.29, 0.46

Table II

Reaction Rate Constants for Hair Fiber Segments Reduced With Either 1 M ATG, 1 M ATG + 0.125 M DTDG, or 1 M ATG + 0.250 M DTDG at pH 9.0 at 23°C

Treatment	$k^* 10^3 (s^{-1})$ (Mean, SD)
1 M ATG	4.41, 0.31
1 M ATG + 0.125 M DTDG	4.48, 0.24
1 M ATG + 0.250 M DTDG	3.42, 1.08

ATG, ammonium thioglycolate.

DTDG, dithiodiglycolic acid.

#### THE EFFECT OF ADDITION OF DITHIODIGLYCOLIC ACID ON FIBER STRENGTH

To investigate the effect of DTDG on the degree of fiber weakening, fibers from the same source were again divided into three 30-mm treatment sites that were rotated among treatment groups. The fibers were reduced for 5, 10, or 15 minutes in 10 ml of solution and rinsed with distilled water. The mean 20% index was then determined for each treatment. The results of these measurements (Table III) indicated that similar degrees of fiber weakening resulted when the fibers were reduced for 5, 10, or 15 minutes under 1.5% constant strain without neutralization.

The effect of DTDG on fiber strength after neutralization was also investigated. Fibers were reduced for 5, 10, or 15 minutes, rinsed in distilled water, and neutralized for 5 minutes. The results of the mean 20% index determination for each treatment group (Table III) indicated that addition of DTDG affects the strength of the fiber after neutralization. For the fibers that were reduced for 5 or 10 minutes and neutralized, the results indicated that fiber strength increased as the concentration of DTDG added to the reducing solution was increased. However, fibers that were reduced for 15 minutes and neutralized exhibited 20% index values that were not significantly different.

Table III

Comparison of 20% Index for Hair Fibers Reduced With Either 1 M ATG, 1 M ATG + 0.125 M DTDG, or 1 M ATG + 0.250 M DTDG at pH 9.0 and 23°C for a Specific Time Length

Treatment	Reduction time (min)	20% Index without neutralizer	20% Index with neutralizer
1	5	0.70 ± 0.08	0.68 ± 0.05
	10	0.40 ± 0.04	0.61 ± 0.05
	15	0.36 ± 0.04	0.70 ± 0.14
2	5	0.63 ± 0.11	0.80 ± 0.09
	10	0.42 ± 0.04	0.71 ± 0.04
	15	0.40 ± 0.02	0.73 ± 0.09
3	5	0.64 ± 0.08	0.79 ± 0.17
	10	0.43 ± 0.05	0.75 ± 0.08
	15	0.41 ± 0.03	0.72 ± 0.15

All values reported are the mean of six measurements:

Treatment 1: 1 M ammonium thioglycolate.

Treatment 2: 1 M ammonium thioglycolate + 0.125 M dithiodiglycolic acid.

Treatment 3: 1 M ammonium thioglycolate + 0.250 M dithiodiglycolic acid.

## DISCUSSION

### EFFECT OF PH VARIATION ON THE REACTION RATE CONSTANT OF HAIR REDUCED BY ATG

It has been established that the redox potentials of thiol compounds increase with pH and that increasing the pH of the solution also affects the reaction rate constant,  $k$ . This trend has been shown by Wickert for reduction of human hair by sodium thioglycolate (1) and by Weigmann for the reduction of wool fibers by 1,4-dithiothreitol (9). Similarly, in this study, the reduction of human hair by ammonium thioglycolate was found to be dependent on pH (Table I). A 1 M ATG solution reduced hair more rapidly at pH 9.5 (which is nearest the  $pK_{SH}$  of 10.4) than the same solution at either pH 9.0 or 8.0. Sodium thioglycolate has been observed to exhibit pseudo first-order kinetic behavior at  $pH < 10$  (1). Ammonium thioglycolate, which differs from sodium thioglycolate only by the type of cation, also exhibited pseudo first-order kinetic behavior at  $pH < 10$ .

### EFFECT OF DITHIODIGLYCOLIC ACID ON REACTION RATE CONSTANT OF HAIR REDUCED BY ATG

The effect of the addition of DTDG on the reaction rate constant of hair reduced by ATG was studied in order to determine if the reduction of keratin was affected. More specifically, this condition was investigated to determine if DTDG was a competitive or blocking agent for the disulfide interchange mechanism.

Speakman *et al.* (15,16) have demonstrated that stress relaxation of keratin fibers occurs in two distinguishable steps. The first step is the breakage of hydrogen bonds, van der Waals interactions, and salt linkages (17,18). The second step is the rate-determining breaking of disulfide bonds. Weigmann *et al.* (5,7) have shown that in the presence of both reducing agents and increased temperature disulfide bonds are transformed into energetically favored positions (i.e., stress-free positions) through a disulfide interchange reaction with sulfhydryl groups. Furthermore, Weigmann *et al.* (5,7) have demonstrated by use of an SH-blocking reagent that the disulfide interchange mechanism dominates the second step of stress relaxation. Therefore, in the presence of a blocking reagent, the interchange mechanism cannot proceed, and structural rearrangement leading to stress relaxation does not occur. This would be observed as a decrease in the rate of stress relaxation of the fiber.

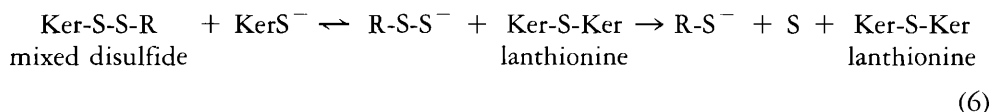
The results from this present study indicate the effects of addition of DTDG on the kinetics of stress relaxation of hair by 1 M ATG at pH 9.0 are not significant. From the observed reaction-rate constants for hair fibers reduced under immersion conditions having 1.5% strain applied, the effect produced by the addition of 0.125 M DTDG on the reaction rate constant was not statistically significant. The same was true for the addition of 0.250 M DTDG to a 1 M ATG solution at pH 9.0.

At low extension rates, stress is almost exclusively supported by the disulfide bonds in the fiber, which are displaced by an interchange mechanism with existing thiol groups into stress-free positions (5). This interchange mechanism results in rapid stress relaxation of the fiber. If DTDG behaved as a blocking or competitive reagent, a decrease in the reaction-rate constant for stress relaxation would have been observed. Therefore, we propose that DTDG is not a competitive reagent, as the addition of DTDG to solutions of ATG does not affect the kinetics of stress relaxation when the fiber is held under 1.5%

strain, and as all three treatments exhibited pseudo first-order kinetics and similar reaction rate constants were observed.

#### MECHANISM FOR REDUCTION OF HAIR BY AMMONIUM THIOGLYCOLATE WITH DITHIODIGLYCOLIC ACID

The mechanism of disulfide reduction by mercaptans (thiols) has been shown to proceed through two displacement reactions (Eqs. 1a and 1b). In 1958, Schöberl and Gräfe (19) proved that the first displacement reaction (Eq. 1a) leads to the formation of the mixed disulfide of keratin and mercaptan. Later, in 1974, Boré and Arnaud (20) confirmed that nucleophilic substitution occurs in the second displacement reaction (Eq. 1b) and indicated that another pathway may exist (Eq. 6):

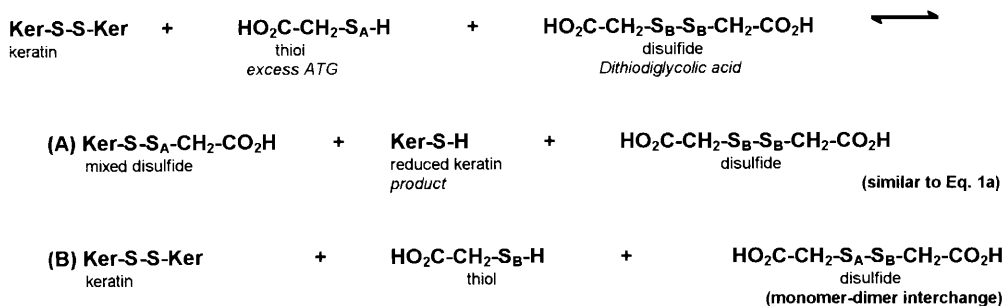
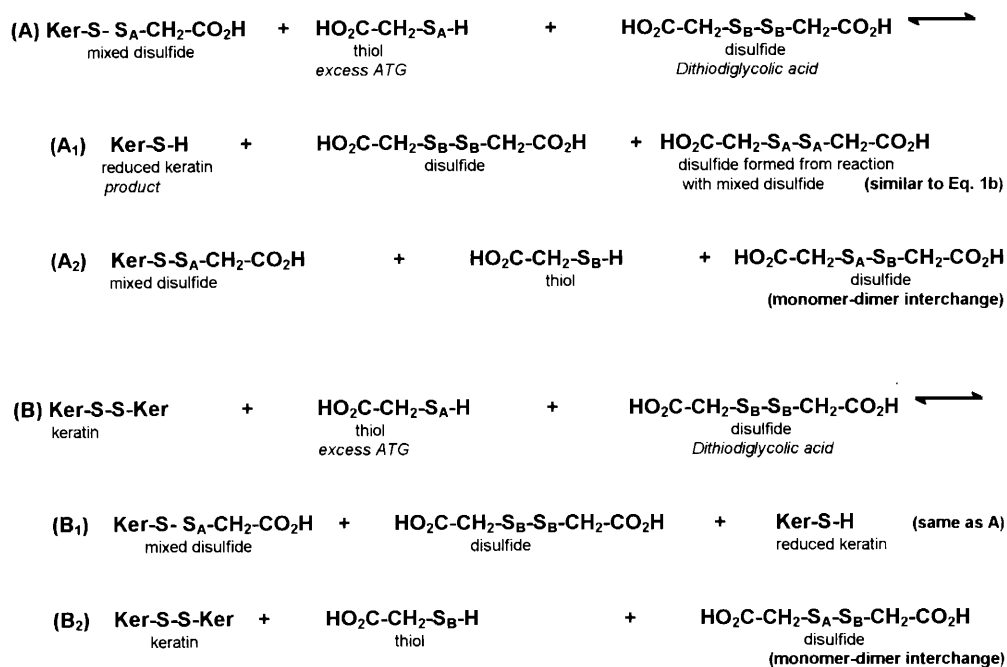


The mechanism of reduction of hair by a solution of ammonium thioglycolate with dithiodiglycolic acid is thought to be more complex as the number of intermediate pathways is increased. Upon examination of such a system, the potential competitive reduction pathways for this system may be proposed (Scheme 1). The first nucleophilic substitution by the mercaptide ion, RS, may proceed through either of two pathways, given as (A) or (B). The pathway designated as (A) resembles that of Equation 1a, while (B) is simply a monomer–dimer interchange. Both pathways (A) and (B) may participate in the second nucleophilic substitution by a second mercaptan ion as given by (A<sub>1</sub>), (A<sub>2</sub>), (B<sub>1</sub>), and (B<sub>2</sub>). The pathway designated (A<sub>1</sub>) resembles Equation 1b, while pathway (A<sub>2</sub>) is a monomer–dimer interchange. Pathway (B<sub>1</sub>) is the same as (A), whereas pathway (B<sub>2</sub>) is nothing more than a monomer–dimer interchange.

Theoretically, the probability of the monomer–dimer interchange pathway predominating should increase as the concentration of DTDG in the solution is increased. However, this is not the case, as the monomer–dimer interchange is not the rate-determining step of the reaction. According to the pseudo first-order kinetic model, the rate-determining step is the slow reduction of the disulfide bonds in keratin by the reducing agent. Therefore, the monomer–dimer interchange pathway may be neglected in this system, and the system simplifies to that of the reduction of keratin by a mercaptan as given by Equations 1a and 1b.

#### EFFECT OF ADDITION OF DITHIODIGLYCOLIC ACID ON FIBER STRENGTH

In order to determine if the addition of DTDG to an ATG solution limits the extent of fiber reduction, the fiber strength was assessed after various times (5, 10, or 15 minutes) using the 20% index. The 20% index ratio is a measure of the force at 20% extension after treatment versus the force at 20% extension before treatment. Values of the 20% index near 1 indicate that the fiber is essentially unchanged, while values near zero indicate a greater degree of fiber weakening. The results (Table III) indicate that similar degrees of fiber weakening occurred for all three treatments at equivalent times. This indicates that the extent of stress-supporting disulfide bond reduction was not limited as determined by SFTK results when the fiber was held under 1.5% strain.

**First Nucleophilic Substitution:****Second Nucleophilic Substitution:**

Scheme 1.

However, hair fibers that were reduced in the presence of DTDG for 5 or 10 minutes were stronger after neutralization, as determined by the 20% index (Table III). No significant difference was found for hair fibers neutralized after 15 minutes of reduction in the presence of DTDG versus reduction in ATG alone. This effect of DTDG on fiber strength following neutralization may be due to a higher formation of mixed disulfide during the reduction step (Ker-S-S-CH<sub>2</sub>-COOH), which may be more easily converted to native keratin (Ker-S-S-Ker) rather than to cysteic acid or lanthionine.

**CONCLUSIONS**

1. The addition of increasing amounts of exogenous disulfide may reduce overprocessing

by limiting the extent of reduction of the disulfide bonds via a competitive reaction. However, the kinetics of stress relaxation were not affected when the fiber is held under 1.5% constant strain, because all three treatments exhibited pseudo first-order kinetics and produced similar reaction rate constants.

2. The addition of dithiodiglycolic acid did not significantly alter the chemical kinetics of stress relaxation or diminish the extent of fiber weakening prior to neutralization as indicated by the 20% index ratio. However, hair reduced in the presence of dithiodiglycolic acid was stronger after neutralization.

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