

Rate of Crosslinking of Gelatin in Aqueous Solution*

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Synopsis

The rate of crosslinking of concentrated gelatin solutions in water has been measured by means of a gelation timer. Some effects of temperature, pH, crosslinking agent, and gelatin concentration have been measured. The crosslinking agents have varied from fast-acting chrome alum, glutaraldehyde, and a carbodiimide to slow-acting mucobromic acid and dialdehyde starches. Detailed crosslinking mechanisms are discussed for dimethylol urea, mucobromic acid, and several dialdehyde crosslinking agents. Some effects of urea and other additives on the dimethylol urea crosslinking rate are described.

INTRODUCTION

The rate of crosslinking of gelatin in aqueous solution is important in the manufacture of photographic silver halide gelatin emulsions. A gelatin crosslinking agent, i.e., gelatin hardener, is usually added to an emulsion to increase the resistance of the coated emulsion to swelling and softening during processing. Viscosity changes during the coating of the liquid emulsion must be minimized. The purpose of this paper is to report some quantitative data on the variables controlling the crosslinking rate in aqueous solution. The use of a gelation timer is a relatively new technique. The kinetics of crosslinking of gelatin using viscometry have also been recently reported.¹

In the work reported here, the experimental procedure will be described first. Then a working hypothesis for the kinetics of crosslinking will be given. The effects of gelatin concentration, temperature, and pH will be described along with results obtained for a variety of crosslinking agents.

EXPERIMENTAL

By using a Techue gelation timer [Techne (Cambridge) Ltd., Duxford, Cambridge, England], the setting time of a gelatin solution was measured after the addition of a cross-linking agent. The temperature was so chosen that the solution would not set without the addition of crosslinking agent. A description of the instrument by the manufacturer is as follows. A weighted disk immersed in the solution is subjected to a simple harmonic vertical motion, with a period of 1 min., by connection to a geared syn-

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chronous motor. As the solution sets, a point is reached at which the stiffness is sufficient to support the weight of the disk during a 30-sec. half cycle. Up to this point, the connecting link has been under tension both during the up and down strokes, but as soon as the disk is supported, the link on its down stroke becomes subjected to a compression causing an electric contact in the link to close a circuit. This in turn opens a relay irreversibly, stops the synchronous motor, and lights a small neon lamp, to attract attention. The gelation time, in minutes, is then read off on the counter.

For the purpose of this test, when the gelatin/crosslinking agent solution acquires a stress relaxation time of 30 sec., it is said to have gelled or set. A recent detailed analysis² of the instrument showed that gelation of other polymeric systems corresponded closely to an infinite network. Since the number of crosslinks required for an infinite network will depend on the molecular weight, degradation of gelatin during measurements could have an effect on hardener induced gelation time. However, it is believed that this effect can be neglected for the conditions reported below.

The gelatin solution was made up by adding, with stirring, the required amount of gelatin into the required amount of distilled water. After stirring for 10 min. at room temperature to allow the gelatin to swell, the mixture was heated to 50°C. until the gelatin was dissolved and then the solution was cooled until set and refrigerated. As needed, the gel was melted at the temperature to be used. The measurement was carried out by adding 200 g. of gelatin solution to a 250-ml. bottle immersed in a constant temperature ($\pm 0.05^\circ\text{C}$.) bath. An 8-ml. portion of hardener solution was added in 5-10 sec. while the solution was stirred mechanically. The stirring was continued for 1 min., and then the piston of the gelation timer was immersed in the solution. The timer was then started. The gelation time was taken as the timer reading plus the time between hardener addition and starting of the clock. All gelatin concentrations in this paper are in per cent by weight before the addition of hardener.

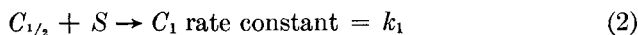
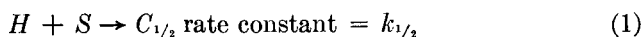
Gelatin Characteristics

All of the results reported below were obtained with bone gelatin. Unless otherwise stated, the gelatin was the same bone gelatin (No. 6). It has a Bloom rigidity value of 246 g. The viscosity of the Bloom solution at 60°C. is 48.4 mpoise. The pH of a 1% solution at 35°C. is 6.08. The isoelectric point from measurement of the viscosity of a 1% solution as a function of pH is 4.95 ± 0.1 . The viscosity-average molecular weight was 93,300. This was calculated from published³ values of the Mark-Houwink constants and the measured value of the intrinsic viscosity, which was 0.411 dl./g. in 0.2*N* acetate buffer at 35°C. The weights of gelatin were not corrected for moisture. No buffers were used in the hardening experiments; thus, the initial pH of all gelatin solutions is approximately 6 unless otherwise stated.

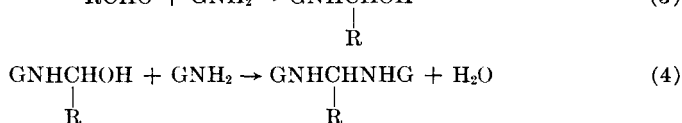
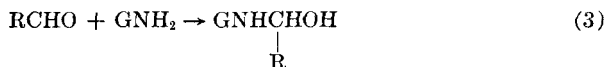
CROSSLINKING HYPOTHESIS

While the mechanisms of crosslinking of gelatin are not actually known,¹ it is useful to have the following working hypothesis to derive a relationship between initial hardener concentration and gelation time. Let us define H_0 = initial concentration of crosslinking agent, H = concentration of crosslinking agent at time t , S_0 = initial concentration of crosslinkable sites, S = concentration of crosslinkable sites at time t , $C_{1/2}$ = concentration of half links at time t , C_1 = concentration of crosslinks at time t , a = number of sites per crosslink, $\rho = aC_1/S_0$ = crosslink density, ρ_g = crosslink density at time $t = t_g$, i.e. at gelation time.

Crosslinking is assumed* to occur stepwise with two sites per crosslink as follows:



For aldehyde hardening, these reactions may be:



where GNH_2 represents gelatin.

The rate eqs. (5)–(7) follow:

$$dH/dt = k_{1/2}H^a S^r \quad (5)$$

$$dC_{1/2}/dt = k_{1/2}H^a S^r - k_1 S^m C_{1/2}^n \quad (6)$$

$$dC_1/dt = k_1 S^m C_{1/2}^n \quad (7)$$

If reaction orders are unity and $S \cong S_0$, i.e., very few sites consumed at gelation, then

$$H = H_0 e^{-k_{1/2} S_0 t} \quad (5a)$$

$$C_{1/2} = [H_0 k_{1/2} / (k_1 - k_{1/2})] (e^{-k_{1/2} S_0 t} - e^{-k_1 S_0 t}) \quad (6a)$$

$$C_1 = H_0 \{ 1 + [1 / (k_{1/2} S_0 - k_1 S_0)] [k_1 S_0 e^{-k_{1/2} S_0 t} - k_1 S_0 e^{-k_1 S_0 t}] \} \quad (7a)$$

for the case that at $t = 0$; $H = H_0$, $S = S_0$, $C_{1/2} = C_1 = 0$.

$$d\rho/dt = (a/S_0)(dC_1/dt) = (a/S_0)k_1 S_0^m C_{1/2}^n \quad (8)$$

$$\rho_g = \int_0^{t_g} d\rho = (ak_1/S_0) \int_0^{t_g} S^m C_{1/2}^n dt \quad (9)$$

If most of the hardener molecules have reacted to form half links at $t = t_g$, then $C_{1/2} \cong H_0$. That is, it is assumed that the half-linking re-

* There are, of course, other possibilities such as reaction between two half links to form a crosslink, the reaction with a trifunctional hardener, etc.

action is very fast ($k_{1/2} = \infty$) and crosslinking is a very slow ($k_1 = 0$). Then eq. (9) gives:

$$t_g \approx (\rho_g/ak_1S_0^{m-1})(1/H_0^n) \quad (10)$$

or

$$t_g \approx k/H_0^n \quad (11)$$

where

$$k = \rho_g(ak_1S_0^{m-1})^{-1}$$

Thus, in this case, the gelation time (alternatively k) is inversely proportional to the rate constant for crosslinking, k_1 .

RESULTS AND DISCUSSION

It was found that the dependence of t_g on H_0 agreed very well with eq. (11) for many hardeners and it is thus a useful empirical relationship. However, it applies only for sufficiently large values of H_0 since there will be a minimum concentration of hardener required for gelation. Equation (11) could not be verified for fast-acting hardeners where the linear portion of the plot of $\log t_g$ versus $\log H_0$ corresponds to gelation times of less than 1 min. Examples are glutaraldehyde and chrome alum in 10–20% gelatin. The quantities k and n are experimentally accessible by determining the

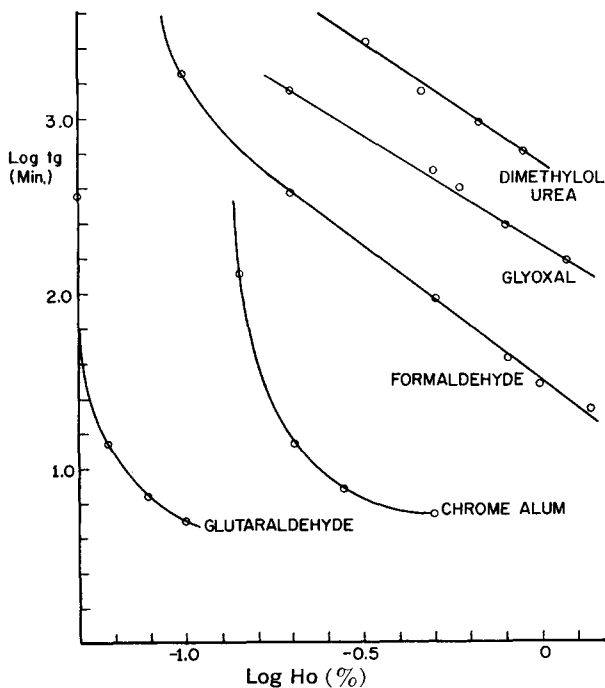


Fig. 1. Effect of hardener concentration on gelation time of 10% gelatin at 35°C.

value of $\log t_g$ at $H_0 = 1$ and the slope of a log-log plot of t_g and H_0 . Figure 1 shows typical plots at 35°C. A summary of the hardening rate parameters at 45°C. is shown in Table I.

TABLE I
Summary of Gelation Rate Data for Gelatin Hardeners^a
 $t_g = k/H_0^n$

Hardener	n	k for H_0 , wt.-%	k for H_0 , moles/l.
2-Hydroxyadipaldehyde	3.2	3800	292
Eponite 100 ^b	0.66	832	—
Mucochloric acid	0.82	562	33.2
Mucobromic acid	0.98	135	5.3
Dimethylol urea	1.80	47.8	3.98
Glyoxal	1.84	15.8	2.73
Formaldehyde	1.76	1.95	0.65
Aldocryl X-12 ^c	1.58	2.4	0.58
<i>p</i> -Benzoquinone	0.88	5.9	0.55

^a Dimensions of k depend on dimensions of H_0 and t_g . All results for 20% gelatin by weight at 45°C. and t_g in minutes.

^b Shell Chemical Company trademark for a polymeric diepoxide.

^c Shell Chemical Company trademark for a low molecular weight acrolein condensate. k for H_0 in moles/liter was calculated by using a value of 41.6 as the carbonyl equivalent weight.

Effects of Different Gelatins on Dimethylol Urea-Induced Gelation Time

In order to determine how the results might depend on the particular gelatin used, a number of gelatins were compared under the same conditions. Table II shows the dimethylol urea hardening rate parameters for 20% gelatin at 45°C. for a series of different gelatins. All of the gelatins in Table II are bone gelatins of isoelectric point of $\pm 9.5 \pm 0.1$. Gelatin No. 6 is the gelatin described above.

TABLE II
Effect of Different Gelatins on the Dimethylol Urea Hardening Rate Parameters in 20% Gelatin at 45°C.

Gelatin no.	ϵ -Amino, meq./g. ^a	pH of 4.5% Solution at 40°C.	Viscosity-average molecular weight ^b	$k(H_0 \text{ in } \%)$	n
1	0.41	5.35	93,300	2400	1.92
2	0.49	5.31	—	2820	1.82
3	—	—	—	1700	1.58
4	0.41	5.58	95,500	2070	1.66
5	0.50	5.79	—	872	1.64
6	0.55	6.05	93,300	47.8	1.80

^a Determined by the titration method of Kenchington and Ward.⁴ The gelatins were not deionized or dried.

^b Data of Pouradier and Venet.³

The large differences in k values appear to be due to the small differences in pH and primary amino content rather than to molecular weight differences. The n values are similar to values obtained¹ for the rate exponent of the dependence of the rate of viscosity increase on formaldehyde concentration.

Effect of Temperature on Gelation Time

It is possible to derive a simple relationship between gelation time and temperature in order to calculate the activation energy for crosslinking.

If it is assumed that the Arrhenius relationship holds between the crosslinking rate constant and temperature, then

$$k_1 = Ze^{-E_a/RT} \quad (12)$$

where Z = frequency factor, T = absolute temperature, R = gas constant, and E_a = activation energy.

If it is assumed that t_g is inversely proportional to k_1 as in eq. (10), then

$$t_g = A/k_1 \quad (13)$$

where A depends on kinetics, crosslink density as shown in eq. (11).

Combining eqs. (12) and (13) gives:

$$t_g = (A/Z)e^{E_a/RT} \quad (14)$$

or combining eqs. (11) and (14) gives:

$$k = (H_0^n A/Z)e^{E_a/RT} \quad (14a)$$

Therefore a plot of $\log k$ versus $1/T$ should be a straight line of slope $E_a/2.303R$ and intercept $\log (H_0^n A/Z)$. Such results have been reported by others^{5,6} for the effect of temperature on the gelation rate of other systems during crosslinking. Results for formaldehyde and dimethylol urea were obtained by calculating k and n in eq. (11) for t_g in minutes and H_0 in per cent by weight. This was done at five temperatures. Then $\log k$ was plotted against $1/T$ as shown in Figure 2. E_a and $\log (H_0^n A/Z)$ were calculated by least squares from the slope and intercept. Note that $(H_0^n A/Z)$ has the same dimensions as k . Typical results are shown in Table III.

TABLE III
Activation Energy From Gelation Time Measurements

Hardener	Gelatin No. 6 concentration,		E_a , cal./mole	$H_0^n A/Z$
	wt.-%			
Dimethylol urea	10	15,400	6.60×10^{-9}	
Formaldehyde	10	17,350	1.74×10^{-11}	
Formaldehyde	20	17,300	2.29×10^{-12}	

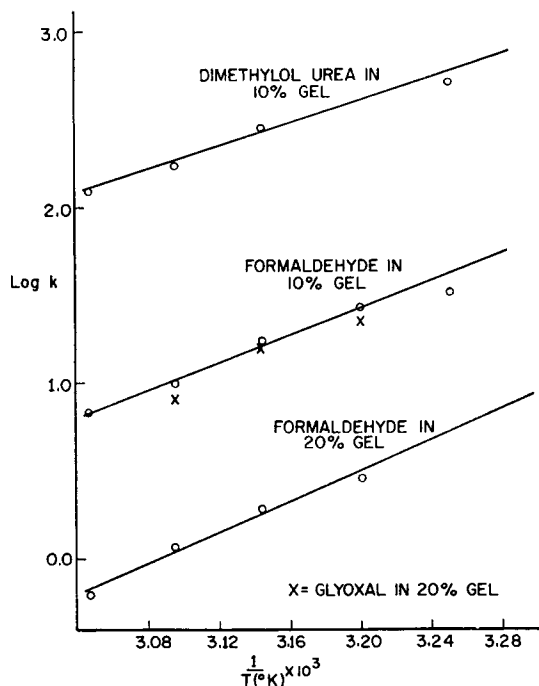


Fig. 2. Effect of temperature on hardening rate of (O) dimethylol urea in 10% gelatin, formaldehyde in 10% gelatin, and formaldehyde in 20% gelatin; (X) glyoxal in 20% gelatin.

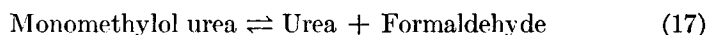
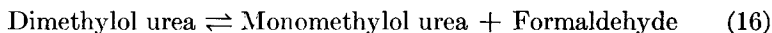
Results for glyoxal in 20% gelatin were obtained at only 40, 45, and 50°C. However, the activation energy is very close to that for formaldehyde and ($H_0^n A/Z$) is about 10^{-11} . It was found that in 20% gelatin at 35°C, the gelation times were faster than expected from extrapolation of results at temperatures above 40°C. This can be explained by the gelation of gelatin itself at 35°C.

The lower value of ($H_0^n A/Z$) for formaldehyde at higher gelatin concentrations reflects the lower value of A/Z , since n was independent of gelatin concentration. For the special case of equation (10),

$$A = \rho_0 (a S_0^{m-1} H_0^n) \quad (15)$$

Thus A should decrease as S_0 is increased, i.e., as the gelatin concentration is increased. Increasing the gelatin concentration from 10 to 20% increased A/Z by a factor of 7.5. This is similar to results using viscometry¹ in which the rate of formaldehyde crosslinking depended on the gelatin concentration to the 2.3 to 2.7 power.

The difference in activation energies for formaldehyde and dimethylol urea can be explained by the equilibria of eqs. (16) and (17).



It can be shown that

$$C_F^2 = K_1 K_2 (C_d/C_u) \quad (18)$$

where C_F = concentration of formaldehyde, C_d = concentration of dimethylol urea, C_u = concentration of urea, K_1 = equilibrium constant for reaction (16), and K_2 = equilibrium constant for reaction (17).

If one assumes that the active crosslinking agent in dimethylol urea is formaldehyde, then eqs. (14) and (18) give:

$$\log k = (n/2) [\log(K_1 K_2) + \log(C_d/C_u)] + \log(A/Z) + E_a/RT \quad (19)$$

Data^{7,8} on the effect of temperature on these equilibrium constants show that they increase with temperature.

Assuming that the van't Hoff temperature-equilibrium constant equation holds, i.e.,

$$\log K_1 = -\Delta H_1^\circ/RT + C_1 \quad (20)$$

and

$$\log K_2 = -\Delta H_2^\circ/RT + C_2 \quad (21)$$

where ΔH_1° is the standard enthalpy change for reaction (16), ΔH_2° is the standard enthalpy change for reaction (17), and C_1 and C_2 are integration constants. Then,

$$\begin{aligned} \log k = (n/2) [C_1 + C_2 + \log(C_d/C_u)] + \log(A/Z) \\ + [E_a - (n/2)(\Delta H_1^\circ + \Delta H_2^\circ)]/RT \quad (22) \end{aligned}$$

Thus the apparent activation energy for dimethylol urea is smaller than formaldehyde by the amount $(n/2)(\Delta H_1^\circ + \Delta H_2^\circ)$. In support of this view that dimethylol urea is only a formaldehyde reservoir is the fact that the values of n in Table I are the same for formaldehyde and dimethylol-urea.

Effects of Urea on Dimethylol Urea Hardening Rate

In order to see if the gelation time for a dimethylol urea solution agreed with the gelation time of a formaldehyde solution of concentration calculated from eq. (18), a formaldehyde buffer was made up consisting of equal moles of urea and dimethylol urea. The gelation time in 10% gelatin at 35°C. was measured and compared with the gelation time of a formaldehyde solution of the concentration calculated from eq. (18). Values of 0.2 and 0.032 were used for K_1 and K_2 , respectively.⁸ As an approximation, it was assumed that C_d/C_u was constant and that very little of the formaldehyde was consumed before gelation. The measured and calculated values were 4004 and 5880 min., respectively. Figure 3 shows the steepness of the gelation time/urea concentration curve. Thus, considering the approximations, fair agreement was obtained.

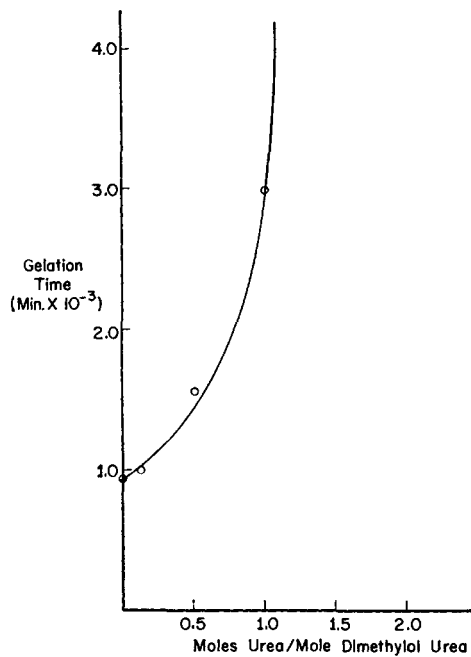


Fig. 3. Effect of urea on hardening rate of dimethylol urea in 10% gelatin at 35°C.

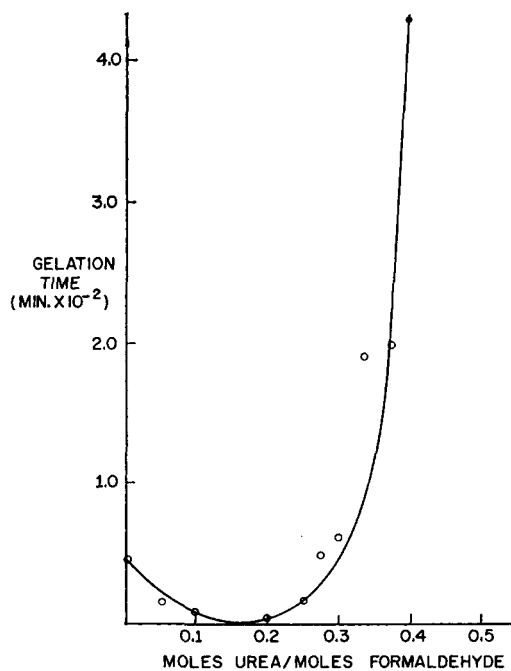


Fig. 4. Effect of urea on hardening rate of formaldehyde in 10% gelatin at 35°C. (0.493 mole formaldehyde/100 g. gelatin).

Effect of Urea and Other Additives on Formaldehyde Hardening Rate

A surprising acceleration of formaldehyde hardening of 10% gelatin at 35°C. was observed when low concentrations of urea were added to the gelatin before the addition of formaldehyde as shown in Figure 4. A possible explanation is that urea is also reacting with gelatin so as to render amino groups more accessible to formaldehyde. At a sufficiently high concentration of urea, the effect is obscured by the reaction of urea and formaldehyde. Interestingly enough, no such acceleration was observed

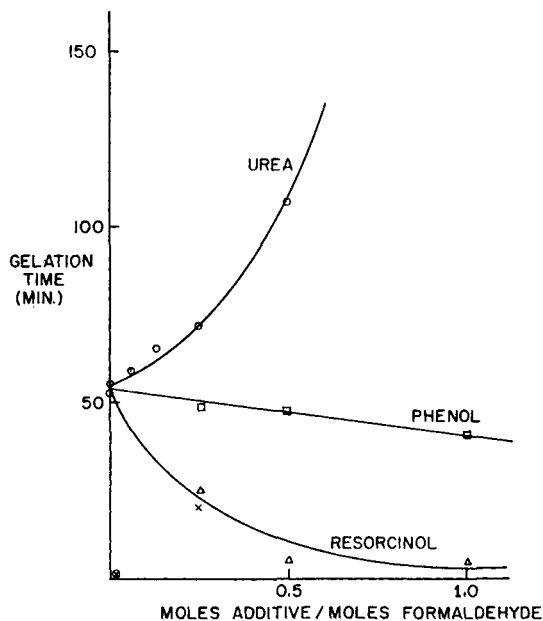


Fig. 5. Effect of additives on hardening rate of formaldehyde in 20% gelatin at 45°C.: (O) urea; (□) phenol; (Δ) resorcinol; (⊗) phloroglucinol; (×) *m*-methoxyphenol.

at 45°C. in more concentrated solution. This suggests that the acceleration involves disruption of gelatin hydrogen bonds by urea at 35°C., since little hydrogen bonding would be expected at 45°C.

Figure 5 shows the effects of other additives on formaldehyde hardening at 45°C. In the series phenol, resorcinol, phloroglucinol, an increasing acceleration of hardening with formaldehyde was observed. The reason for this acceleration is not known, but it is possible that the reaction product of formaldehyde with these hydroxybenzene compounds is a faster acting hardener than formaldehyde itself. It is also possible that these compounds react with gelatin at 45°C. The fact that *m*-methoxy phenol and resorcinol show the same amount of acceleration suggests that the electron density on the unoccupied positions of the benzene ring is a key factor.

Effect of pH on Formaldehyde Hardening Rate

The effect of pH on the formaldehyde hardening rate is shown in Figure 6. This represents the combined effect of pH on the ionization of the amino groups and on the conformation of gelatin. As the pH is changed from the isoelectric point, there is a buildup of uncompensated charge on the gelatin and the chains expand, presumably increasing the distance between cross-linkable sites. However, as the pH is raised, the amount of free amino groups increased. The side chain-protonated amino groups in gelatin

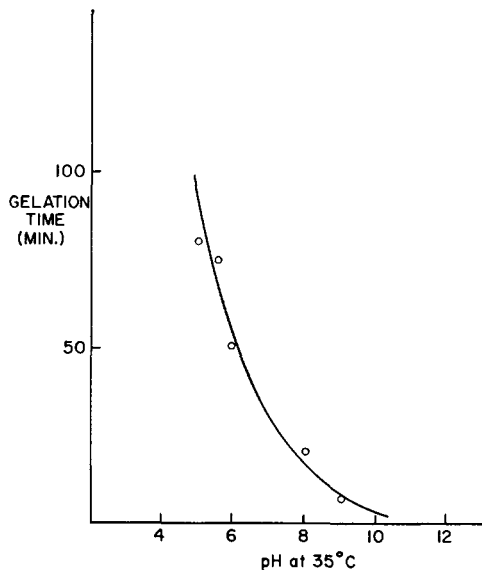
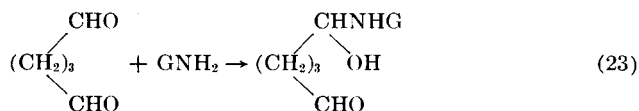


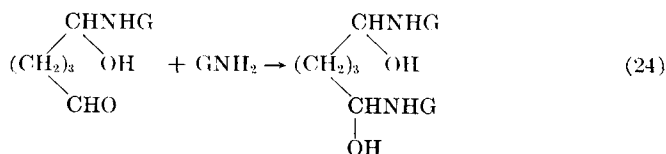
Fig. 6. Effect of pH on hardening rate of formaldehyde in 10% gelatin at 35°C. (0.33 mmole/100 g. gelatin).

ionize⁴ to the free base in the pH range 8–11.5 at 40°C. Figure 6 shows that the ionization effect dominates the chain expansion effect and the hardening rate with formaldehyde increases rapidly as the pH is raised and appears to be leveling off at around pH 10 or 11.

Relative Hardening Rates of Dialdehyde Hardeners

Figure 1 shows that glutaraldehyde is a much faster hardener than glyoxal. A possible reason is that glutaraldehyde may form a longer link than glyoxal with a resulting greater probability of completing the cross-link with the second aldehyde group as shown in eqs. (23) and (24).





Another possibility is that if the glutaraldehyde half link can react with another amino group via a Schiff base, then glutaraldehyde might be a tetrafunctional crosslinking agent as shown in eq. (25).

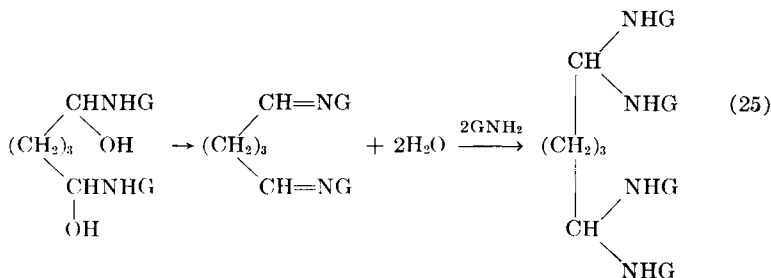
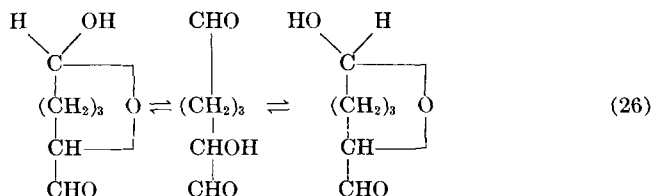


Table I shows that 2-hydroxyadipaldehyde was one of the slowest hardeners tested. Since it is a long-chain dialdehyde, one might expect it to be comparable in rate to glutaraldehyde. However, the slow action may be explained by postulating an oxide structure like a glucoside [eq. (26)].



Several dialdehyde starches were tested, and the results are shown in Table IV. It can be seen that the hardening rate depends on the aldehyde content, i.e., the degree of oxidation of the original starch.

TABLE IV
Summary of Gelation Rate Parameters for Gelatin Hardeners
in 10 wt.-% Gelatin at 35°C.

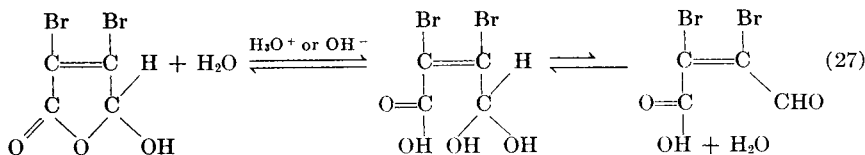
Hardener	n	k for H_0 in wt.-%	k for H_0 moles/l. ^a
Dimethylol urea	1.5	1515	126
Sumstar R* dialdehyde starch ^b	1.4	575	35.7
Glyoxal	1.3	258	44.2
Sumstar S* dialdehyde starch ^b	1.4	240	15.2
Formaldehyde	1.9	79.5	26.5

^a k for H_0 in moles/l. was calculated by using 161 and 158 as values for equivalent weight respectively.

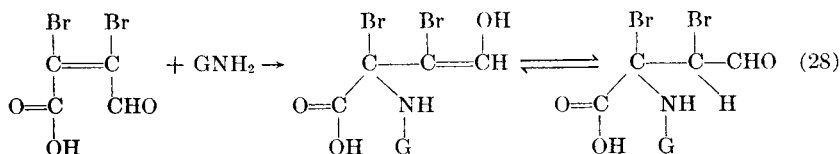
^b Miles Chemical Company trademark. Sumstar R is approximately 75% oxidation and Sumstar S is approximately 90% oxidation of starch.

Hardening Rate of Mucobromic Acid and Related Compounds

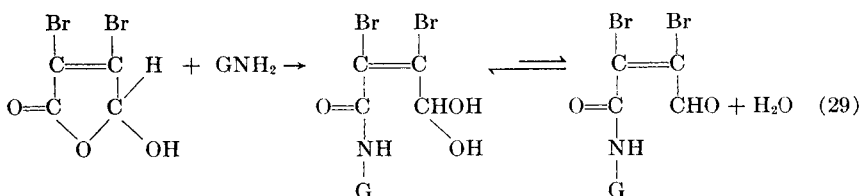
Mucobromic and mucochloric acids probably exist in three forms, the ring, the hydrate and free aldehyde, the proportions depending on pH and water content.⁹⁻¹¹



Conventional aldehyde crosslinking seems possible but two other possibilities exist. Both possibilities have a reactive aldehyde on the end of a longer half link and thus might have a greater probability of crosslinking. One is a 1,4-Michael addition¹² of the gelatin amino group as shown in eq. (28).



The resulting aldehyde (hydrate) would also be capable of conventional aldehyde crosslinks with amino groups. Another possibility¹³ is that the ring form can react with gelatin to form an amide, as shown in eq. (29).



Likewise, the resulting aldehyde can react further with amino groups.

The hardening rate of mucobromic and mucochloric acid in solution is relatively slow as shown in Table I. However, in gelatin films mucochloric acid is a relatively fast-acting hardener, approaching glutaraldehyde.¹³ This can be explained by the hydrate formation in water solution. In dry film, the equilibrium favors the free aldehyde, presumably the active crosslinking group. In support of this hypothesis, mucobromic acid (or its half links) would be expected to have more free aldehyde than mucochloric acid and indeed mucobromic acid is a faster hardener.

The effect of pH on the hardening rate of gelatin by mucobromic acid is shown in Figure 7. The hardening rate was found to be a maximum at neutral pH. This would support the ring-opening mechanism, since the addition of acid or base would be expected to decrease the concentration of the ring form. However, this does not prove the ring-opening mechanism,

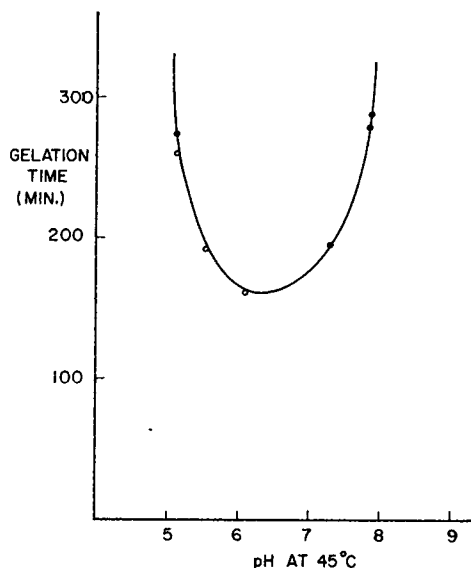
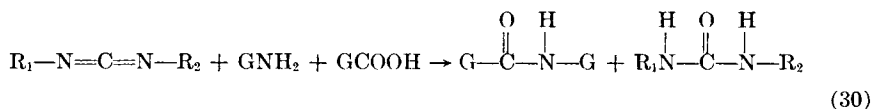


Fig. 7. Effect of pH on hardening rate of mucobromic acid in 20% gelatin at 45°C. (9.77 mmole/100 g. gelatin).

and more evidence is needed, since there may be several mechanisms operative at once.

Hardening Rate of Gelatin With A Carbodiimide

One of the fastest gelatin hardeners tested was 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride.* The net reaction is probably¹⁴ as given in eq. (30).



As with other extremely fast-acting gelatin hardeners such as chrome alum and glutaraldehyde, the concentration of carbodiimide which might obey eq. (11) corresponds to gelation times under 1 min., the shortest time measurable by the timer. Table V shows how much faster the carbodiimide is than formaldehyde.

In conclusion, the gelation timer is a useful tool for studying the rate of crosslinking of gelatin solutions. Variations in chemical structure of some of the crosslinking agents can reasonably account for differences in crosslinking rates.

* A sample was kindly provided by Prof. J. C. Sheehan, M.I.T. A second sample was obtained from the Ott Chemical Co.

TABLE V
Comparison of Gelatin Hardening Rates of Carbodiimide and Formaldehyde in 20%
Gelatin No. 6 at 45°C.

Hardener	H_0 , mmole/100 g. gelatin	t_g , min.
Carbodiimide	2.09	∞
"	5.22	987
"	6.53	68
"	7.32	1
Formaldehyde	16.7	120
"	25	51
"	33.3	31
"	50	15

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References

1. Davis, P., and B. E. Tabor, *J. Polymer Sci.*, **A1**, 799 (1963).
2. Hills, B. A., *J. Oil Colour Chemists Assoc.*, **45**, 251 (1962).
3. Pouradier, J., and A. M. Venet, *J. Chim. Phys.*, **47**, 391 (1950).
4. Kenchington, A. W., and A. G. Ward, *Biochem. J.*, **58**, 202 (1954).
5. Gough, L. J., and I. T. Smith, *J. Appl. Polymer Sci.*, **3**, 362 (1960).
6. Negishi, N., Y. Nakamura, and T. Koide, *J. Polymer Sci.*, **62**, 241 (1960).
7. Landquist, N., *Acta Chem. Scand.*, **9**, 1466, 1471 (1955).
8. DeJong, J. I., J. De Jonge, and H. A. K. Eden, *Rec. Trav. Chim.*, **72**, 88 (1953).
9. Vinogradova, E. I. and M. M. Shemyakin, *J. Gen. Chem. USSR (Engl. transl.)*, **16**, 709 (1946).
10. Dury, K., *Angew. Chem.*, **72**, 864 (1960).
11. Mowry, D. T., *J. Am. Chem. Soc.*, **72**, 2535 (1960).
12. Suggested by Professor J. C. Sheehan, M.I.T.
13. Schoenthaler, A. C., private communication.
14. Albertson, N. F., *Organic Reactions*, Vol. XII, Wiley, New York, 1962.

Résumé

La vitesse de pontage de solutions concentrées de gélatine dans l'eau a été mesurée en employant un mesureur de gélatine. On a déterminé les effets de la température, du pH, de l'agent de ramification ainsi que de la concentration en gélatine. Comme agents de ramification, on en a employé plusieurs depuis les plus actifs, comme l'alun de chrome l'aldéhyde glutarique et un carbodiimide jusqu'aux plus faibles tels l'acide mucobromique et les amidons dialdéhydes. Des mécanismes détaillés de ramification ont été discutés pour la diméthyl urée, l'acide mucobromique et plusieurs agents de pontage dialdéhydiques. On a décrit certains effets de l'urée et d'autres additifs sur la vitesse de pontage par la diméthylurée.

Zusammenfassung

Die Vernetzungsgeschwindigkeit von konzentrierten Gelatine-lösungen in Wasser wurde gemessen. Der Einfluss von Temperatur, pH, Vernetzungsmittel und Gelatinekonzentration wurde bestimmt. Eine Reihe von Vernetzungsmitteln vom rasch wirkenden Chromalaun, Glutaraldehyd und einem Carbodiimid bis zu langsam wirkender

Brommuconsäure und Dialdehydstärke wurde verwendet. Der Vernetzungsmechanismus wird für Dimethylolharnstoff, Brommuconsäure und einige Dialdehydvernetzer in den Einzelheiten diskutiert. Der Einfluss von Harnstoff und anderen Zusätzen auf die Vernetzungsgeschwindigkeit mit Dimethylolharnstoff wird beschrieben.

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