

of the further ultraviolet absorption of boiled aqueous solutions of form A may suggest hydrolysis. On account of the inconclusive evidence concerning the question of the slow hydrolysis of the B form, it is not possible at present to associate the spectral observations with the details of the chemical changes and the problem requires further investigation.

Finally a suggestion may be made on the origin of the different melting points of the two forms. Gluconitrile may resonate between the structures  $RC:::N:$  and  $RC^+::\ddot{N}^-$  as the alkyl cyanides are supposed to do.<sup>13</sup> The rather ionic character of the CN group might then lead to the formation of hydrogen bonds between the highly electro-negative hydroxyl oxygen and the nitrogen atoms. According to Thompson's infrared investigations<sup>14</sup> intermolecular bonding is more prominent in liquid hydroxy nitriles. As the presence of intermolecular hydrogen bridges is associated with higher melting points than their absence,<sup>13</sup> it seems plausible to associate the high melting point of the A form with the presence of intermolecular hydrogen bonds, while in the B form the bonds are either weaker or of the intramolecular type. More direct information on this question might be gained from a study of the infrared spectra of appropriate gluconitrile derivatives in which all but one hydroxyl group is blocked.

The author wishes to express his thanks to Dr. Wm. F. Ehret for the X-ray work, to Dr. Wm.

(13) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 183-84, 270-272, 300-314.

(14) Thompson, *THIS JOURNAL*, **61**, 1396 (1939).

West for the use of the spectrograph, to Dr. Raymond L. Garman and Dr. Marcel E. Droz for the microphotometer curves, and to Mr. D. Rigakos for the micro-analyses.

### Summary

The two forms of gluconitrile, A and B, melting at 145 and 120.5°, respectively, shown by earlier work to differ in their optical activity, exhibited, within the accuracy of the measurements, the same X-ray powder diffraction spectra, but different ultraviolet absorption spectra. Aqueous solutions of the B form displayed an absorption band at 2780 Å. and an extinction coefficient given by  $\log \epsilon_{\text{molar}} = 0.9$ , approximately. The (ultraviolet) spectrum also underwent complex changes with time. The A form gave a spectrum resembling that of  $\beta$ -hydroxypropionitrile and showing no absorption maximum at  $\lambda$  2780 Å. Several cyclic compounds containing carbonyl or imino groups, derivable from the nitrile, are regarded as causing the band at 2780 Å. Interconversion of these compounds may be responsible for the changes with time in the details of the characteristic band, and for the changes in optical rotation as well as for other spectral changes in the short wave ultraviolet. A gradual hydrolysis of the B form would not account for some facts and degradation by loss of hydrogen cyanide was shown to be inconsiderable. Consideration was given to the possibility that the two crystalline forms A and B differed in the nature of the hydrogen bonding.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 877]

## Hydration of Unsaturated Compounds. XI. Acrolein and Acrylic Acid<sup>1</sup>

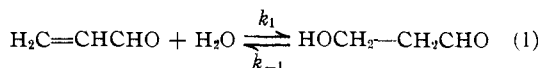
BY D. PRESSMAN AND H. J. LUCAS

**Kinetics.**—The hydration of acrolein<sup>2</sup> is shown by Eq. 1. That of acrylic acid<sup>3</sup> is similar.

(1) Previous communication, X, *THIS JOURNAL*, **64**, 1122 (1942).

(2) J. U. Nef has shown that acrolein undergoes hydration in hot aqueous solution to form hydracrolein, *Ann.*, **335**, 219 (1904). Hydration of acrolein in aqueous sulfuric acid can explain the results of Lobry de Bruyn, who isolated a colorless syrup, probably hydracrolein, from a dilute aqueous sulfuric acid solution of acrolein, *Rec. trav. chim.*, **4**, 232 (1885).

(3) Acrylic acid undergoes hydration in aqueous sodium hydroxide, E. Lennemann, *Ber.*, **8**, 1095 (1875); E. Erlenmeyer, *Ann.*, **191**, 281 (1878). Hydracrylic acid undergoes dehydration in 50% sulfuric acid, W. Moldenhauer, *ibid.*, **131**, 335 (1864); J. Wislicenus, *ibid.*, **166**, 23 (1873).



At a given hydronium ion concentration in dilute aqueous solution, the hydration is first order with respect to the unsaturated compound and the dehydration is first order with respect to the hydrated compound, as shown by the straight line character of the plots of  $\log_{10} \epsilon/(\epsilon - x)$  against  $t$  (Fig. 1), which is the case of two first order reac-

tions coming to an equilibrium, according to the integrated Eq. 2

$$\log_{10} \epsilon / (\epsilon - x) = t(k_1 + k_{-1}) / 2.303 \quad (2)$$

Here  $x$  is the fraction of the original unsaturated compound hydrated at time,  $t$ ,  $\epsilon$  is the fraction hydrated at equilibrium and  $k_1$  and  $k_{-1}$  are the specific first order rate constants of hydration and dehydration, respectively, at a given hydronium ion concentration.

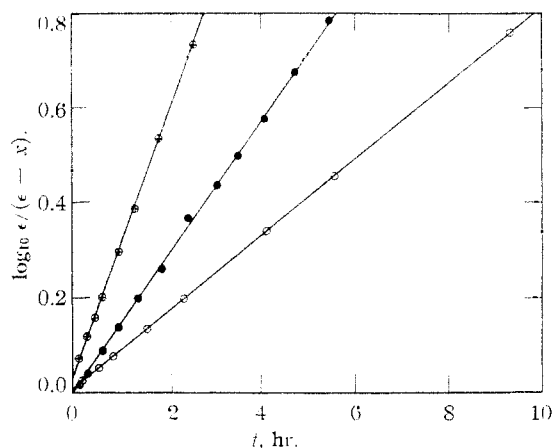


Fig. 1.—Hydration of acrolein and acrylic acid, dehydration of hydracrylic acid:

Starting compound	Temp., °C.	(H <sub>3</sub> O <sup>+</sup> ), N	$\frac{\mu}{N}$
○ Acrolein	29.20	0.493	0.493
● Acrylic acid	119.8	1.01	2.00
⊕ Hydracrylic acid	119.8	1.92	2.00

The individual values of  $k_1$  and  $k_{-1}$  were calculated from the values of  $(k_1 + k_{-1})/2.303$ , the slope of the curves of the type of those of Fig. 1, and the equilibrium constant, Eq. 3.

$$K = k_1 / k_{-1} = \epsilon / (1 - \epsilon) \quad (3)$$

All of the values of  $\epsilon$  are experimental except the one for acrylic acid at 119.8°, which is calculated from the values at 110.6 and 134.8 by the use of the Arrhenius equation. In Table I are listed the values of  $k_1$ ,  $k_{-1}$ ,  $\epsilon$  and  $K$  for acrolein and acrylic acid.

The reversibility of the hydration-dehydration system was demonstrated in each case by lowering the temperature after the system had already reached equilibrium and then returning the system to the original temperature after equilibrium had been established at the lower temperature. The system returned to the original equilibrium. In each case the extent of hydration was greater at the lower temperature, thus showing that the equilibrium could be approached from both sides and demonstrating the exothermic character of the hydration reaction.

The reversibility in the case of acrylic acid was confirmed by observing the rate of dehydration of hydracrylic acid at 119.8°. The values thus obtained for  $k_1$ ,  $k_{-1}$ ,  $\epsilon$  and  $K$  agree well with values from the hydration experiments. The two systems are remarkable in the stability of the equilibrium. Evidently the  $\beta$ -hydroxy compound is the only reaction product in these two cases.

The effect of replacing sodium ion by hydronium ion is evident from the slight decrease in the values of  $k_1/(\text{H}_3\text{O}^+)$  and  $k_{-1}/(\text{H}_3\text{O}^+)$ , (Table 1), and of the equilibrium constants  $K$ . Undoubtedly these effects are due primarily to the presence of oxonium complexes, as was demonstrated previously in the case of the mesityl oxide-diacetone alcohol system.<sup>1</sup> The decreases in  $k_1/(\text{H}_3\text{O}^+)$  and  $k_{-1}/(\text{H}_3\text{O}^+)$  probably are due to the fact that each oxonium complex is less reactive than the uncomplexed compound. The decreases in the equilibrium constants probably are due to the fact that each hydrated compound is a weaker base than the respective unsaturated compound. The roles of the oxonium complexes were not investigated further.

**Thermochemistry.**—The heats of activation of the hydration and dehydration reactions were calculated by means of the Arrhenius equation. The heats of activation in the temperature range 19.98 to 29.70° are: for the hydration of acrolein, 18.0 kcal. in 0.249 *N* perchloric acid and 17.5 kcal. in 0.493 *N* acid; for the dehydration of hydracrolein, 24.0 kcal. in 0.249 *N* acid and 24.5 kcal. in 0.493 *N* acid. The heats of activation, 110.6 to 119.8°, are: for the hydration of acrylic acid, 20.4 kcal. in 1.01 *N* acid and 20.2 kcal. in 2.00 *N* acid; for the dehydration of hydracrylic acid, 27.0 kcal. in 1.01 *N* acid and 26.8 kcal. in 2.00 *N* acid.

It is probable that the heat of activation of the complexed form approximates that of the uncomplexed form, since the heat of activation is essentially constant even though the hydrogen ion concentration changes.

Values of  $\Delta H$  for the hydration reactions were obtained from plots of  $\log K$  against  $1/T$ . For the hydration of acrolein in 0.249 *N* acid three points fell on a straight line, giving for  $\Delta H$  the value of  $-5.8$  kcal. and at 0.493 *N* acid two points gave  $-5.8$  kcal., while the third point, at 19.98°, was inconsistent. For the hydration of acrylic acid in 1.01 *N* and 2.00 *N* acid,  $\Delta H$  is  $-6.5$  and  $-6.7$  kcal., respectively.

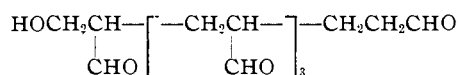
TABLE I  
KINETIC DATA

Temp., °C. ±0.03	(H <sub>2</sub> O <sup>+</sup> ), N	Unsatd. compd., initial M	$\epsilon$	$K$	$k_1 + k_{-1}$	$k_1$ , hrs. <sup>-1</sup>	$k_{-1}$ , hrs. <sup>-1</sup>	$k_1/(H_2O^+)$	$k_{-1}/(H_2O^+)$
Acrolein-Hydracrolein at Ionic Strength 0.493 N									
19.98	0.249	0.0337	0.9234	12.08	0.0366	0.0338	0.00281	0.136	0.0113
19.98	.493	.0342	.9236	12.00	.0693	.0640	.00530	.130	.01075
29.70	.249	.0350	.896	8.62	.1015	.091	.01054	.365	.0424
29.70	.493	.0350	.892	8.26	.1885	.168	.0204	.341	.0414
39.93	.249	.0329	.865	6.41					
39.93	.493	.0234	.861	6.20					
Acrylic Acid-Hydracrylic Acid at Ionic Strength 2.00 N									
±0.2									
110.6	1.01	0.0375	0.9195	11.40	0.177	0.163	0.0143	0.161	0.0142
110.6	2.00	.0502	.9184	11.23	.341	.313	.0279	.157	.0140
119.8	1.01	.0375	(.903) <sup>a</sup>	(9.37) <sup>a</sup>	.338	.305	.0327	.302	.0325
119.8	2.00	.0502	(.902) <sup>a</sup>	(9.17) <sup>a</sup>	.643	.580	.0633	.290	.0317
134.7	1.01	.0375	.873	6.88					
134.7	2.00	.0502	.870	6.69					
119.8 <sup>b</sup>	1.92	.084 <sup>b</sup>	.905	9.5	.622	.564	.059	.288	.0306

<sup>a</sup> Calculated by interpolation. <sup>b</sup> Reaction started with hydracrylic acid.

The replacement of hydronium ion by sodium ion appears to have no effect on the heat of hydration. This would be expected if the uncomplexed and complexed forms of the unsaturated compound have identical heats of hydration, as was noted in the case of mesityl oxide.<sup>1</sup>

**The Hydration of Acrolein in Water.**—Nef<sup>2</sup> observed that hydracrolein was formed when a 25% solution of acrolein was heated in a sealed tube at 100°, and that the yield decreased, due to polymerization, if the heating was continued longer than seventy hours. Recently Rodebush<sup>4</sup> and co-workers have measured the absorption spectra of aged aqueous acrolein solution, and have found that they are quite similar to the absorption spectrum of aqueous aldol. They claim that the material responsible for the characteristic absorption is a polycondensation product similar in nature to the hydrated pentamer which Gilbert and Donleavy<sup>5</sup> consider to be the product resulting from the polycondensation of acrolein in dilute aqueous alkaline solutions and to which they assign the structure



The arguments advanced by Rodebush, *et al.*, in substantiation of their claim are: (1) similarity in absorption spectra of aqueous aldol and aged acrolein solutions; (2) structural resemblance between aldol and the pentamer of Gilbert and

(4) A. M. Buswell, E. C. Dunlop, W. H. Rodebush and J. B. Swartz, *THIS JOURNAL*, **62**, 328 (1940).

(5) E. Gilbert and J. Donleavy, *ibid.*, **60**, 1737 (1938).

Donleavy, in that both are  $\beta$ -hydroxyaldehydes; (3) absence of absorption due to a conjugated double bond, as would be the case if acrolein underwent the aldol condensation, which it is not known to do anyway. They completely overlook the possibility of a simple hydration of acrolein to hydracrolein, which explains in a highly satisfactory manner the effects they observed. On this account it became desirable to investigate the hydration of acrolein in water, in the absence of a catalyst.

Experiment showed that 0.03 M aqueous acrolein solution after heating at about 100° gave, at successive intervals, the following fractions of unchanged acrolein: 0.6 hr., 0.88; 1.3 hr., 0.715; 3.3 hr., 0.433; 7.5 hr., 0.395; 23 hr., 0.391. The equilibrium value 0.39 is close to 0.411 and 0.416, the values obtained when aliquots of a solution 0.02 M in acrolein and 0.5 N in perchloric acid were heated in boiling water for five and thirteen minutes, respectively, before quenching.<sup>6</sup> It appears from these results that in water at 100° the acrolein comes to a fairly stable equilibrium with hydracrolein, which is known to be formed in this solution.<sup>2</sup>

At 29.70 and 19.98° it was possible to follow the reaction more closely than at 100°. From the nature of the curves obtained by plotting  $x$  and  $\log x$  against  $t$ , Fig. 2, it is evident that the reaction is essentially first order with respect to acrolein. The nature of the curves seems to indicate

(6) Even after two and one-half hours of heating, the value is 0.392, showing the stability of the system.

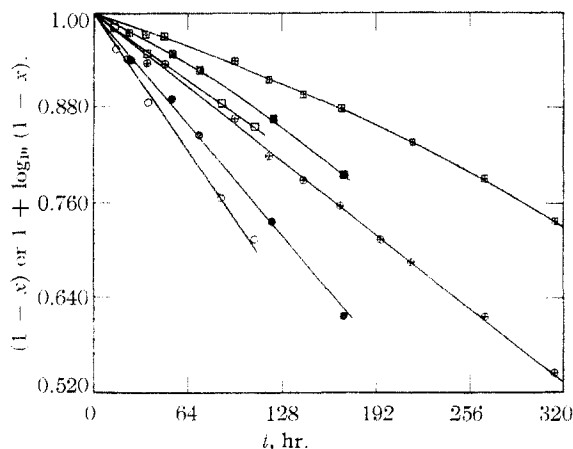


Fig. 2.—Hydration of acrolein in pure water, plot against time of  $(1 - x)$  and  $1 + \log_{10}(1 - x)$ :

Temp., °C.	Initial concn., M	Plot of $(1 - x)$	Plot of $1 + \log_{10}(1 - x)$
30	0.0340	○	□
20	0.0338	△	◇
20	0.0316	●	■

that the rate constant increases as the reaction proceeds. This is due to cumulative evaporation losses into the free space above the solution. As this space becomes larger the percentage loss by evaporation increases, thus giving the effect of a continually accelerating reaction. This effect was not observed in the acid-catalyzed studies because the loss due to evaporation was negligible in comparison to decrease of acrolein through hydration.

Non-reproducibility of the hydration data in water points to an extreme sensitivity to catalysis as, for example, slight daily variations in the pH of the water. In any event, the rate of hydration in water is negligible, when compared to the rate in acid solution.

### Experimental

**Acrolein.**—Eastman Kodak Co. acrolein was distilled immediately before use. Determination of unsaturation by bromine absorption showed 1:000 double bond per mole. The analysis was carried out with an acetic acid solution, since acrolein is miscible with this solvent. Thus it is possible to make up a solution quantitatively by weight.

**Acrylic Acid.**—This was prepared by the action of metallic zinc upon a refluxing aqueous solution of  $\alpha,\beta$ -dibromopropionic acid.<sup>7</sup> The fraction of acrylic acid which distilled at 138–140° and melted at 8° was purified by freezing about half way and decanting the liquid. After four such treatments the acid melted at 10.3°. When debromination was carried out without external heating, the boiling point of the acrylic acid was 140.0–0.3°, and the melting point of the distilled acid was 11.0°. This higher melting point when debromination is carried out at the lower tem-

perature is due to the fact that there is less propionic acid present. The presence of propionic acid is indicated by the fact that whereas the neutralization equivalent as determined by titration with standard base was low by 2% (probably due to evaporation losses) bromine absorption was low by 5%.

**Calcium Hydracrylate.**—Hydracrylic acid was prepared by Mr. Frank Dickey from ethylene cyanohydrin.<sup>8</sup> After purification by ether extraction from the aqueous solution, it was shaken with a paste of calcium hydroxide and water. The resulting liquid was made neutral to phenolphthalein with carbon dioxide. Following removal of insoluble material by filtration, the solution of calcium hydracrylate was concentrated to a viscous mass in a vacuum desiccator. This was dried at 75° in an Abderhalden dryer. The resulting white deliquescent powder gave negative tests for chloride and sulfate ions with silver and barium nitrate solutions, respectively. *Anal.* Calcd. for  $C_6H_{10}O_6Ca$ : Ca, 18.4. Found: Ca (by ashing), 18.98, 19.02.

**Analysis.**—Acrolein was determined by the bromine absorption technique described previously in connection with crotonic acid.<sup>9</sup> Bromine was absorbed as rapidly as it was liberated from the bromate–bromide mixture. There was no interference from any hydracrolein present.

Acrylic acid reacted so slowly that after ten minutes, with 150% excess of bromide, only 90% of the theoretical amount of bromine was absorbed. On the addition of aqueous mercuric sulfate (so that the ratio of the concentration of mercuric ion<sup>10</sup> to the final concentration of bromide ion was about 1.3), absorption of bromine was quantitative after two minutes, with 50% excess bromine. Substitution was negligible. Actually this was only 4% in twenty-five minutes, even when the excess of bromine was 400%. Hydracrylic acid did not interfere. Substitution here was comparable to that in the dibromo acid.

**Procedure.**—For runs at 100° or above, the organic material was added to the acid or water, aliquots were sealed in ampoules and then placed in the thermostat at the required temperature. Ampoules were removed from time to time, quenched in cold water and analyzed. For runs at 40° or lower, acrolein was added to water or aqueous acid solution in a flask at the proper temperature. Immediately after thorough mixing an aliquot was analyzed. Other aliquots were removed at various intervals of time.

Correction was made for the change in hydrogen ion concentration when calcium hydracrylate was added.

No correction was made for the change in volume when the organic material was dissolved in the aqueous solution, usually about 1 ml. per liter, since any error is so small (about 0.1%) that it can be neglected. No account was taken of the change in concentration with temperature, since the equilibria and, hence, the heats of hydration are not affected.

### Summary

The equilibria in aqueous perchloric acid solutions in the systems, acrolein–hydracrolein, and acrylic acid–hydracrylic acid, have been studied.

(8) "Organic Syntheses," Coll. Vol. I, J. Wiley and Sons, Inc., New York, N. Y., 1932, p. 314.

(9) D. Pressman and H. J. Lucas, *THIS JOURNAL*, **61**, 2271 (1939).

(10) H. J. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

(7) Billman, *J. prakt. Chem.*, [2] **61**, 491 (1900).

The rates of hydration and dehydration are first order with respect to hydronium ion and to the organic compound involved.

In each case the drop in the values of the specific reaction rate constants of hydration and dehydration when hydronium ion replaces sodium ion is ascribed to the formation of an oxonium complex which is less reactive than the uncomplexed compound.

In each case the decrease in the value of the

equilibrium constant with the above change is ascribed to the fact that the unsaturated compound probably is a stronger base than the corresponding hydrated compound.

Acrolein hydrates at 100° in pure water and in 0.5 *N* perchloric acid to the same extent.

The values for  $\Delta H$  of hydration are: -5.8 kcal. in the case of acrolein, and -6.6 kcal. in the case of acrylic acid.

PASADENA, CALIF.

RECEIVED APRIL 6, 1942

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

## Studies on Reactions Relating to Carbohydrates and Polysaccharides. LXV. An Improved Technique for the Fractionation of Partially Methylated Glucosides<sup>1</sup>

BY IRVING LEVI, W. LINCOLN HAWKINS AND HAROLD HIBBERT

The quantitative separation of mixtures of partially methylated glucosides obtained on hydrolysis of methylated polysaccharides has been attempted by three general methods.<sup>2,3,4</sup> Several of the techniques described during recent years have been complicated, requiring large amounts of the methylated polysaccharide, and no procedure has been reported by which a complete quantitative separation of mixtures of tetra-, tri- and dimethylmethyl glucosides can be effected.

A description is now given of an improved procedure based on the fractionation principles and technique described by Podbielniak.<sup>5</sup> Several control fractionations carried out with mixtures of synthetic 2,3,4,6-tetramethyl-, 2,3,4-trimethyl- and 2,3-dimethylmethyl glucosides yielded excellent separations of the glucosides with a total recovery of 95-97%. The fractionation results on a typical mixture of these glucosides are shown in Table I. With this apparatus the 2,3,4-trimethylmethyl glucosides could be readily fractionated into the pure solid  $\beta$  and the liquid  $\alpha$  isomer. In no case was there any appreciable decomposition.

In a recent investigation<sup>6</sup> on the structure of dextran, the present procedure gave very satisfactory results; an excellent separation was obtained using only three to four grams of the

Fraction	Fraction, g.	OCH <sub>3</sub> , %	"Tetra," g.	"Tri," g.	"Di," g.
1	0.746	60.5	0.746		
2	.151	59.6	.113	0.038	
3	.387	52.5		.387	
4	.665	52.3		.665	
5	.257	52.4		.257	
6	.300	50.8		.249	0.051
7	.451	42.1			.451
Total wt.	2.957		.859	1.596	.502
Starting wt.			.872	1.660	.516

The theoretical methoxyl values for tetra-, tri- and dimethylmethyl glucosides are 62.0, 52.6 and 41.9%, respectively. The amounts of each present in the small intermediate fractions (2 and 6) were calculated on this basis.

mixed glucosides. Intermediate fractions were very small and there was *practically no non-volatile residue* (not more than 1% and in some cases not detectable). The application of this fractionation technique is thus of particular significance in the field of structural carbohydrate chemistry, especially where the amount of material is limited and more than one distillation undesirable.

The fractionating column used is shown in Fig. 1. It is packed with a gold-plated wire (20 gage) spiral with  $1/8$ " pitch. The vacuum-jacket, column head and delivery tube of the small condenser were wound with a heating element (nichrome ribbon) and the small condenser adapted for the passage of cold water or steam, depending on the nature of the distillate.

(1) Original manuscript received August 13, 1941.

(2) Haworth and Macheimer, *J. Chem. Soc.*, 2270 (1932); Haworth and Percival, *ibid.*, 2277 (1932).

(3) Macdonald, *THIS JOURNAL*, **57**, 771 (1935).

(4) Hess and Neumann, *Ber.*, **70B**, 710 (1937).

(5) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931); **5**, 119 (1933).

(6) Levi, Hawkins and Hibbert, *THIS JOURNAL*, **64**, 1959 (1942).