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The Hydration of Unsaturated Compounds. VI. The Rate of Hydration of *trans*-Crotonaldehyde. The Equilibrium between *trans*-Crotonaldehyde and Aldol in Dilute Aqueous Solution[1]

BY SAUL WINSTEIN AND HOWARD J. LUCAS

The conversion of crotonaldehyde to aldol and the more important reverse reaction are well known. Wurtz[2] found that crotonaldehyde in hydrochloric acid solution was transformed to aldol. Numerous methods for the production of crotonaldehyde are based upon the thermal decomposition of aldol, with or without the addition of a catalyst.[3] Although it is evident that an equilibrium is involved in the aldol–crotonaldehyde system, apparently not even approximate data on the equilibrium constant appear in the literature.

Continuing the work on the hydration of unsaturated compounds and extending it to compounds other than hydrocarbons, we have investigated the kinetics of the hydration of crotonaldehyde in dilute aqueous solutions of nitric and perchloric acids.

Materials.—The *trans*-crotonaldehyde[4] was Niacet material twice distilled through a 100-cm. column of glass rings. The middle fraction, b. p. 101.8–102.0° at 744 mm., purity 99.1% by bromine absorption, was used for the hydrations.

Analysis.—The analysis for crotonaldehyde was carried out similarly to the isobutene analysis[5] except that the vacuum technique was unnecessary, an ordinary iodine titration flask being used. The acid was added last and the titration flask could be stoppered before any bromine was liberated from the bromate–bromide solution. In general, there was no variation of results with time of bromination, for analyses in which the crotonaldehyde and the bromine (100% excess) remained together for lengths of time varying from five to thirty minutes yielded results all agreeing within 0.2%.

However, analyses of solutions near equilibrium, *i. e.*, those containing considerable amounts of aldol, did vary with time, more bromine being consumed at longer times. The variation was small, indicating a possible absolute error of 0.3%, in the percentage conversion of the crotonaldehyde. This error was eliminated by using only a small excess of bromate–bromide solution, *i. e.*, an amount equivalent to about 2 ml. of 0.02 *N* thiosulfate. The crotonaldehyde could be accurately and quantitatively determined by brominating for five minutes with this slight excess of bromate, even when acetaldehyde, which it was feared might possibly develop in the solutions, had been added in amounts equivalent to the crotonaldehyde present.

Method.—A crotonaldehyde solution was made up, brought to temperature, and analyzed. Aliquot portions were pipetted into volumetric flasks, diluted almost to volume, proper amounts of nitric or perchloric acids were added, and the volume was adjusted quickly to the final value. The solutions were then kept in glass-stoppered flasks in a thermostat at either 25.0 ± 0.05° or 35.0 ± 0.05°. All the operations were done at constant temperature. Time was counted from the time of the addition of the acid. The initial concentration of crotonaldehyde was known from the analysis of the original stock solution. At suitable times samples were withdrawn and analyzed for crotonaldehyde. The acid concentration of the final solution was determined by titration with standard alkali. In the first runs with nitric acid, the titration with standard base was carried out at the beginning and the end of an experiment. The analyses agreed to within experimental error. No reduction products of nitric acid could be detected.

Stability of Solutions.—Without the addition of acid, aqueous solutions of crotonaldehyde are quite stable. Thus at concentrations of 0.02 and 0.03 *M*, crotonaldehyde at 25° in glass-stoppered bottles showed a decrease of unsaturation of approximately 0.3% in seventy-five hours and the development of acidity corresponding to the oxidation of about 2% of the aldehyde in one month, due to a slow oxidation by traces of oxygen. At 35°, the decrease in unsaturation was only 0.2% during the time that elapsed in a hydration experiment, while oxidation was only 0.5% in seventy-five hours.

Course of Hydration.—When aqueous crotonaldehyde solutions were made acid at 25°, the unsaturation of the solutions decreased relatively rapidly to approximately one-half the original value and then very slowly "drifted" downward, indicating a relatively rapid approach to equilibrium, accompanied by a slow drift. Although somewhat troublesome, this drift was not rapid enough to be very serious.

The drift could have been due to several causes. Ingold[6] found the equilibrium between aldol and acetaldehyde in potassium carbonate solution was completely displaced toward aldol. The solutions were concentrated in aldol. In the present case the solutions were dilute, favoring a slow partial dissociation of the aldol. The odor of acetaldehyde could be detected in the hydrating crotonaldehyde solutions that had stood for some time.

Slow removal of material by further aldol condensations

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[1] For the preceding paper of this series see THIS JOURNAL, **59**, 722 (1937).

[2] Wurtz, *Bull. soc. chim.*, [2] **42**, 286 (1884).

[3] Wurtz, *Compt. rend.*, **87**, 45 (1878); Usines de Melle, German Patent 598,015 (1934); Maude, U. S. Patent 1,738,659 (1929).

[4] Young, THIS JOURNAL, **54**, 2498 (1932).

[5] Lucas and Eberz, *ibid.*, **56**, 460 (1934).

[6] E. H. Ingold, *J. Chem. Soc.*, **125**, 435 (1924).

even at the low concentrations used is also a possible factor contributing to the drift. It is also conceivable that a very small fraction of α-hydroxybutyraldehyde is formed by an irreversible hydration of the crotonaldehyde, giving rise to a slow gradual decrease in the unsaturation of the solution.

Data and Discussion.—When solutions of crotonaldehyde, 0.032, 0.016, and 0.008 *M*, respectively, were made 0.5 *N* in nitric acid, and C_0/C_t (C_0 and C_t being initial and time values of the unsaturation) plotted against the time, *t*, the points for the three solutions fell on the same smooth curve for the first portion of the hydration. This indicated that the rate of hydration is first order with respect to crotonaldehyde and that side reactions of a higher order with respect to crotonaldehyde are negligible. It was possible to obtain values for the specific reaction rate, k_1, by determining initial slopes, but an analytical method was considered better.

Considering the reaction symbolized by equation (1)

$$H_2O + C_4H_6O \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_4H_8O_2 \qquad (1)$$

here k_1 and k_2 are the specific reaction rate constants for the forward and back reactions, respectively, then the integrated expression for the approach to equilibrium, starting with crotonaldehyde, is shown in equation (2) for the case where

$$2.303 \log \epsilon/(\epsilon - x) = (k_1 + k_2)t \qquad (2)$$

the forward and back reactions are first order with respect to crotonaldehyde and aldol, respectively. In the above expression, ϵ represents the fraction of original crotonaldehyde converted to aldol at equilibrium and x denotes the fraction converted at time *t*.

In treating the data of any run, ϵ was varied so as to give the best constancy of $[\log \epsilon/(\epsilon - x)]/t$ neglecting the long time points where the slow drift had affected considerably the values of x.

The data for two typical runs are shown in Tables I and II. The constancy of $[\log \epsilon/(\epsilon - x)]/t$ indicates that the approach to equilibrium follows the unimolecular law. The values for k_1 and k_2 shown were calculated by means of equations (3) and (4)

$$k_1 = \epsilon\,(k_1 + k_2) \qquad (3)$$

$$k_2 = (1 - \epsilon)\,(k_1 + k_2) \qquad (4)$$

It is to be emphasized that the values of k_1 are more accurate than those of k_2, since k_1 is less sensitive to a change in ϵ. The accuracy with which the experimental data were fitted is shown by a comparison between the experimental values of x and those calculated from the chosen ϵ and the derived average $(k_1 + k_2)$. The agreement is within experimental error nearly to equilibrium, but at the larger values of *t*, the agreement is not so good, due to the drift. The order of magnitude of the drift can be seen from the difference in the experimental and calculated values of x, Tables I and II.

TABLE I

HYDRATION OF CROTONALDEHYDE AT 25° IN 1.905 *N* NITRIC ACID

$\epsilon = 0.442$

Time, hrs.	100 x Exptl.	100 x Calcd.	Log $\epsilon/(\epsilon - x)$	$\frac{\text{Log } \epsilon/(\epsilon - x)}{t}$
2.13	8.8	8.7	0.0959	0.0450
4.17	15.3	15.4	.1838	.0441
6.30	21.0	21.0	.2794	.0443
12.60	31.7	32.0	.5488	.0436
23.48	40.3	40.2	1.054	.0448
52.98	46.1	44.0		
100	48.7	44.2		

Mean 0.0444
Per cent. mean deviation 1.0
$k_1 + k_2$ 0.1022 hrs.$^{-1}$
k_1 .0452
k_2 .0570

TABLE II

HYDRATION OF CROTONALDEHYDE AT 35° IN 1.806 *N* NITRIC ACID

$\epsilon = 0.378$

Time, hrs.	100 x Exptl.	100 x Calcd.	Log $\epsilon/(\epsilon - x)$	$\frac{\text{Log } \epsilon/(\epsilon - x)}{t}$
0.41	4.3	4.3	0.0523	0.127
.79	7.8	7.8	.1000	.127
1.22	11.6	11.6	.1593	.130
1.73	15.7	15.3	.2327	.134
2.41	19.6	19.5	.3179	.132
4.04	26.8	26.6	.5359	.132
7.67	34.1	34.0	1.009	.132
24.43	39.6	37.8		

Mean 0.1306
Per cent. mean deviation 1.7
$k_1 + k_2$ 0.300 hrs.$^{-1}$
k_1 .114
k_2 .186

The monomolecular approach to equilibrium for runs covering a range of acid concentrations is shown in Figs. 1 and 2, where $\log \epsilon/(\epsilon - x)$ (ϵ varying slightly in the different runs) is plotted against time.

Table III is a summary of the results of the runs carried to equilibrium. In the runs where μ, the ionic strength, is different from the acid concentration, potassium nitrate was added in amount equal to the difference. $k_1/(H_3O^+)$ and $k_2/(H_3O^+)$ signify the ratio of the specific reaction rate constants, k_1 and k_2, to the acid concentration. The values of k_1, Table III, agree well with the values of k_1 obtained by the method of initial slopes. The mean deviation between the two sets of values in eleven cases was 2.2%

The approximate constancy of $k_1/(H_3O^+)$ and $k_2/(H_3O^+)$ at any one temperature indicates a first order dependence of both the hydration and the dehydration reactions upon the acidity. Therefore, after replacing equation (1) by equation (5)

$$C_4H_6O + H_3O^+ \rightleftarrows C_4H_8O_2 + H^+ \quad (5)$$

k_1, in agreement with the Brönsted theory, is expressed by equation (6), after canceling activity coefficients of two positively charged ions

$$k_1 = k_0\,(H_3O^+)\gamma \qquad (6)$$

Here k_0 is the specific rate constant of hydration adjusted to 1 *N* acid, and γ is the activity coefficient of crotonaldehyde.

The Salt Effect.—Inspection of Table III discloses that with no added salt (Expts. 5 to 17) $k_1/(H_3O^+)$ is constant to several per cent. over the range of acid concentration, in general increasing as the acid concentration decreased. Thus, as the ionic strength increases, $k_1/(H_3O^+)$ decreases, apparently in contradiction to expectations from equation (6). However, comparison of run 4 with 5 or of 3 with 6 discloses that increase of ionic strength by addition of potassium nitrate does increase $k_1/(H_3O^+)$, the increase being of the order of magnitude of the salting out effect one would estimate. Considering runs 1 to 4, it is evident that at constant ionic strength, $k_1/(H_3O^+)$ increases by some 14% as the acid concentration decreases from 2 to 0.5 *N*, the potassium nitrate concentration increasing. These things point to the non-equivalence of the salt effects of nitric acid and potassium nitrate. Since, in the case of isobutene,[5] $k_1/(H_3O^+)$ was constant up to 1 *N* nitric acid, while in this work k_1 is reliable to 2 or 3%, the trends mentioned above deserve notice. Also, in general, ϵ exhibits a trend with acid concentration of the same order of magnitude as the drift in $k_1/(H_3O^+)$ at constant ionic strength. Thus, $k_2/(H_3O^+)$, although somewhat erratic, is constant at constant ionic strength (Expts. 1 to 4) and varies with a change in the ionic strength, increasing as the ionic strength increases. This is the behavior one would expect.

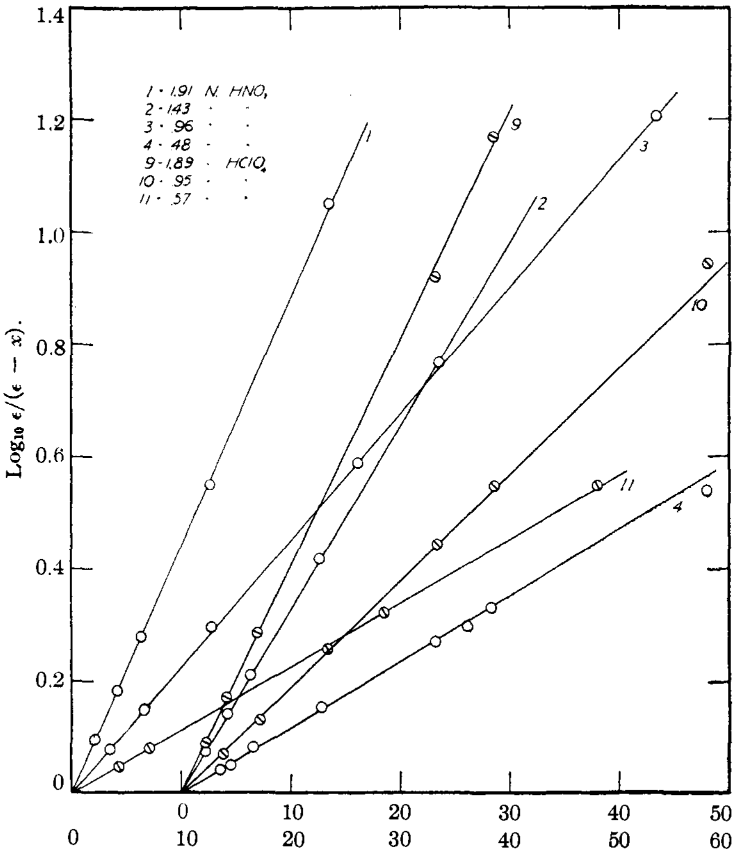

Fig. 1.—Plot of $\log_{10} \epsilon/(\epsilon - x)$ against t for the hydration of crotonaldehyde at 25°.

This can be explained by a "salting in" of the crotonaldehyde by acid, according to a reaction such as is shown in equation (7)

$$C_4H_6O + H_3O^+ \rightleftarrows C_4H_6O{\cdot}H^+ + H_2O \qquad (7)$$

the crotonaldehyde competing with H_2O for the proton somewhat successfully. Thus, as the acid concentration increases, this reaction more than neutralizes the effect of increase of ionic strength. This would explain the trends in $k_1/(H_3O^+)$ and in ϵ, if it can be said that the similar reaction of aldol takes place to a much smaller extent.

A comparison of nitric and perchloric acids shows that rate constants are 6 or 7% lower for the latter than for the former at both temperatures. It is interesting that in the case of the hydrocarbons trimethylethylene[7] and ethyl-

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[7] Lucas and Liu, THIS JOURNAL, **56**, 2138 (1934).

TABLE III

DATA ON THE HYDRATION OF CROTONALDEHYDE AT 25°

No.	Acid	Acid, N	μ	C_0, M	ϵ	$k_1 + k_2$, hrs.$^{-1}$	k_1, hrs.$^{-1}$	k_2, hrs.$^{-1}$	$\frac{k_1}{(H_3O^+)}$, hrs.$^{-1}$	$\frac{k_2}{(H_3O^+)}$, hrs.$^{-1}$
1	HNO_3	1.905	1.90	0.032	0.442	0.1022	0.0452	0.0570	0.0238	0.0298
2	HNO_3	1.432	1.93	.032	.456	.0766	.0350	.0416	.0244	.0291
3	HNO_3	0.9564	1.96	.032	.466	.0523	.0244	.0279	.0255	.0292
4	HNO_3	.4784	1.98	.032	.480	.0270	.0130	.0140	.0272	.0292
5	HNO_3	0.5008	0.50	0.032	0.490	0.0247	0.0121	0.0126	0.0242	0.0252
6	HNO_3	1.004	1.00	.032	.485	.0490	.0238	.0252	.0237	.0251
7	HNO_3	0.5016	0.50	.016	.480	.0254	.0122	.0132	.0243	.0263
8	HNO_3	1.005	1.00	.016	.470	.0511	.0240	.0271	.0239	.0270
								Mean (including 1)	.0240	.0267
9	$HClO_4$	1.886	1.89	0.032	0.440	0.0933	0.0410	0.0523	0.0217	0.0277
10	$HClO_4$	0.9493	0.95	.032	.482	.0440	.0212	.0228	.0223	.0241
11	$HClO_4$	.5697	.57	.032	.497	.0259	.0129	.0130	.0227	.0229
								Mean	.0222	.0249
					At 35°					
12	HNO_3	1.806	1.81	0.032	0.378	0.300	0.114	0.186	0.0632	0.103
13	HNO_3	0.9614	0.96	.032	.390	.1608	.0627	.0981	.0652	.102
14	HNO_3	.4826	.48	.032	.400	.0790	.0316	.0474	.0655	.098
								Mean	.0646	.101
15	$HClO_4$	1.872	1.87	0.032	0.360	0.307	0.111	0.196	0.0593	0.104
16	$HClO_4$	0.7502	0.75	.032	.400	.1131	.0452	.0679	.0602	.091
17	$HClO_4$	.3736	.37	.032	.410	.0564	.0231	.0333	.0618	.089
								Mean	.0604	.095

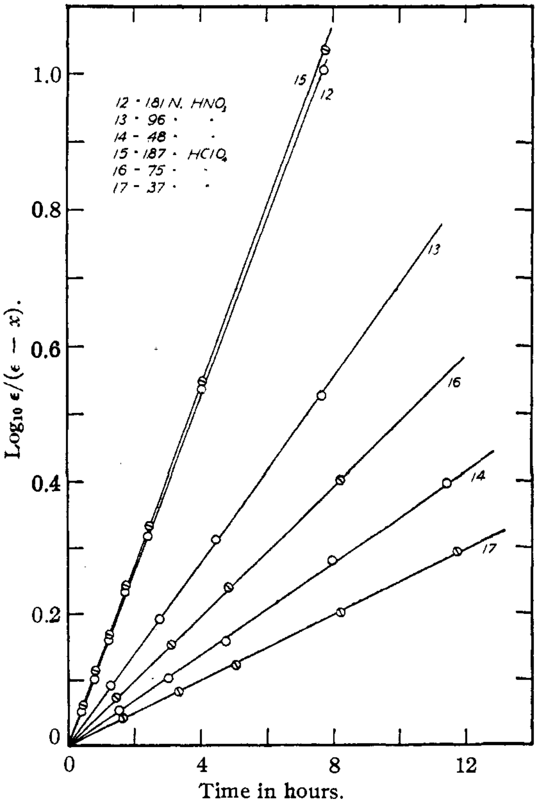

Fig. 2.—Plot of $\log_{10} \epsilon/(\epsilon - x)$ against t for the hydration of crotonaldehyde at 35°.

methylethylene,[8] nitric acid gave lower rates by 5 or 10%.

Temperature Coefficients and Activation Energies.—Table IV gives the temperature coefficients for the forward and back reactions at several approximate concentrations (N) of the two acids, the activation energies of the forward and back reactions (E_1 and E_2, respectively) and the difference ($E_2 - E_1 = -\Delta H$) between these values. The values other than the first set are quite consistent, for the mean deviation in the ΔH value of −6.25 kcal. per mole (excluding the starred value) is only 0.20 kcal. The heat of activation, E_1, of 18.2 kcal. for the hydration is

TABLE IV

TEMPERATURE COEFFICIENTS AND ACTIVATION ENERGIES OF HYDRATION, E_1, AND DEHYDRATION, E_2

Acid	N	$\frac{k_{1\,35}}{k_{1\,25}}$	$\frac{k_{2\,35}}{k_{2\,25}}$	E_1, kcal.	E_2, kcal.	$-\Delta H$ $E_2 - E_1$, kcal.
HNO_3	1.9	2.65	3.46	17.80	22.60	4.80*
HNO_3	0.95	2.74	3.92	18.40	24.90	6.50
HNO_3	0.5	2.70	3.80	18.10	24.40	6.30
$HClO_4$	1.9	2.73	3.76	18.30	24.20	5.90
$HClO_4$	0.85	2.70	3.77	18.10	24.20	6.10
$HClO_4$	0.47	2.72	3.88	18.25	24.70	6.45
Mean		2.72	3.83	18.23	24.48	6.25

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[8] Liu and Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936).

lower than the values for the hydrocarbons, 23.39 for isobutene,[5] 21.04 for methylethylethylene[8] and 18.92 for trimethylethylene.[7] Nevertheless, crotonaldehyde hydrates at a much lower rate, which at 25° is about 1% of that for isobutene. For isobutene ΔH of hydration is -11.56 kcal. per mole.[9] The difference in the values for isobutene and crotonaldehyde can be ascribed perhaps to conjugation energy in the case of crotonaldehyde.

Estimation of Drift Effect.—In order to obtain an estimate of the possible error introduced by the method of treating the data, rate expressions were set up for the cases where the drift was assumed to be due either to a first order disappearance of crotonaldehyde, specific reaction constant being k_3, or to a first order disappearance of aldol, reaction rate constant k_4. The resulting expressions for x as functions of the time are shown in equations (8) and (9)

$$x = 1 + \frac{m_1 + k_2}{m_2 - m_1} e^{m_1 t} - \frac{m_2 + k_2}{m_2 - m_1} e^{m_2 t} \qquad (8)$$

where m_1 and m_2 are the roots of the equation

$$m^2 + (k_1 + k_2 + k_3)m + k_2k_3 = 0$$

$$x = 1 - \frac{m_2 + k_1}{m_2 - m_1} e^{m_1 t} + \frac{m_1 + k_1}{m_2 - m_1} e^{m_2 t} \qquad (9)$$

where m_1 and m_2 are the roots of the equation

$$m^2 + (k_1 + k_2 + k_4)m + k_1k_4 = 0$$

A test was made of the values of k_1 and k_2 in Table III by first choosing k_3 and k_4 so as to give the right magnitude for the drift at the larger values of t, and then varying k_1 and k_2 from the values shown in Table III, so as to obtain the best agreement between x calculated and x observed. When several of the runs were thus treated, k_3 and k_4 amounted to several per cent. of $(k_1 + k_2)$. Assuming that the drift was due entirely to aldol, k_1 was left unaffected, and k_2 tended to increase by as much as 3%. Assuming that the drift was due entirely to crotonaldehyde, k_1 tended to decrease by as much as 3%, and k_2 to increase by as much as 4%; ϵ was therefore reduced by as much as 0.015. These possible corrections were in one direction and did not affect any trends mentioned. In the development of this phase of the work the authors were guided by the advice of Professor R. G. Dickinson, whose aid is gratefully acknowledged.

Hydration of Crotyl Alcohol and Crotonic Acid.—Crotyl alcohol[10] and *trans*-crotonic acid were dissolved in nitric acid solution. The former in 0.6 *N* acid decreased in unsaturation less than 0.2% per day, and the latter in 1.5 *N* acid less than 0.3% per day. It is therefore evident that of the series of compounds having similar structure, *viz.*, 2-butene, crotyl alcohol, crotonaldehyde, and crotonic acid, crotonaldehyde is the only substance which hydrates in dilute aqueous solutions of acids at ordinary temperatures.

Summary

Crotonaldehyde is reversibly hydrated to aldol in dilute aqueous solutions of acids. Hydration is first order with respect to acid and crotonaldehyde. Dehydration of aldol is first order with respect to acid and aldol. Energies of activation for hydration and dehydration are 18.23 and 24.48 kcal., respectively. Equilibrium is reached when 47% of the crotonaldehyde has been converted to aldol at 25° and 39% at 35°.

Crotyl alcohol and *trans*-crotonic acid do not hydrate at an appreciable rate at 25° in dilute aqueous nitric acid.

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[9] Eberz and Lucas, THIS JOURNAL, 56, 1230 (1934).

[10] Kindly supplied by Dr. W. G. Young of the University of California at Los Angeles.