Since the foregoing procedure has given rather low yields (about 22%), an effort will be made in subsequent work to ascertain the conditions for the optimum results. The use of a larger quantity of the dihalogen derivative would doubtless be of great importance.

Summary

A method has been described for the synthesis of the α-methyl-, α-ethyl-, α-*n*-propyl- and α-*n*-butyl-α-phenyl-γ-chlorobutyronitriles. These compounds are being used in the synthesis of Δ^1-pyrrolines and other derivatives.

TROY, N. Y. RECEIVED JULY 11, 1934

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 422]

The Hydration of Unsaturated Compounds. III. The Hydration Rate of Trimethylethylene in Aqueous Solutions of Acids[1]

BY HOWARD J. LUCAS AND YUN-PU LIU[2]

The studies on the hydration of unsaturated compounds which started with isobutene[3] have been extended to trimethylethylene.

Actual hydration of this hydrocarbon by aqueous solutions of formic, acetic and oxalic acids was first observed by Miklaschewsky.[4] Later Michael and Brunel[5] found that in the presence of hydrobromic acid less than 5 *N* the hydrocarbon was converted to the alcohol only.

In the present investigation the rate of hydration of trimethylethylene has been measured at 25 and 35° in the presence of nitric acid and potassium nitrate and at 25° only in the presence of a number of other acids alone.

Experimental

Materials.—The acids used were mostly the ordinary C. P. acids, except the dithionic and *p*-toluenesulfonic acids. The former was prepared by treatment of a known amount of very pure barium dithionate[6] in aqueous solution with the calculated quantity of sulfuric acid, filtering through asbestos with suction and evaporating the filtrate to the desired concentration. Eastman *p*-toluenesulfonic acid was crystallized three times from 6 *N* hydrochloric acid, filtering through sintered glass after decolorizing with norite. The final, colorless crop was allowed to remain in a vacuum desiccator over caustic soda until all hydrogen chloride was gone.

The trimethylethylene was obtained by fractionation of the mixed pentenes resulting from the decomposition of tertiary amyl alcohol when heated with oxalic acid.[7] After four fractionations through an 85-cm. column of glass rings under a reflux, there was obtained a 27% yield of trimethylethylene boiling at 38.2–38.3° (corr.) under 745 mm.

Solutions and Apparatus.—An aqueous solution of trimethylethylene was prepared by shaking 600 ml. of water and 0.5 ml. of the olefin in a tube closed at both ends with stopcocks. The tube remained in the thermostat at 25° until the aqueous phase became clear, a part of the air was removed by suction and the calculated amount of acid added. The contents were throughly mixed by gentle agitation and allowed to stand until the aqueous phase became clear, a matter of several minutes only if the agitation had not been violent. The aqueous solution was then run from the bottom of the container into the reaction apparatus, which was similar to the one previously described[3] except it was larger and had a greater capacity. This previously had been swept out with air saturated with the pentene vapor.

Sampling and Analysis.—These operations were performed as previously described except that a larger sample (18.59 ml.) was taken because the pentene has a lower solubility in water than *i*-butene.

Reaction Product.—This was shown to be the tertiary alcohol as follows: 600 ml. of water saturated with pentene was made 1 *N* in nitric acid and allowed to stand at 25° for three days. The acid was neutralized with sodium hydroxide and the solution was distilled through a fractionating column until the temperature became constant, yielding 10 ml. of a two-phase distillate. The upper phase, after drying with anhydrous potassium carbonate, measured 2 ml. and distilled at 101.5°. On the addition of 10 ml. of concentrated hydrochloric acid a second phase of approximately 2 ml. separated. This distilled at 86°. These boiling points check those of tertiary amyl alcohol and chloride, respectively.

Discussion of the Data

Since it is shown later on that the hydration rate is first order with respect to nitric acid, the hydration of trimethylethylene resembles that of isobutene[3] and may be represented by equation 1.

$$(CH_3)_2C{=}CHCH_3 + H_3O^+ = (CH_3)_2C(OH)CH_2CH_3 + H^+ \quad (1)$$

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(1) Presented at the Berkeley meeting of the American Association for the Advancement of Science, June 20, 1934.

(2) Fellow of the Rockefeller Foundation.

(3) Lucas and Eberz, THIS JOURNAL, **56**, 460 (1934).

(4) Miklaschewsky, *Ber.*, **24**, ref. 269 (1891).

(5) Michael and Brunel, *Am. Chem. J.*, **48**, 270 (1912).

(6) Kindly supplied by Prof. D. M. Yost of this Laboratory.

(7) Norris and Thomson, THIS JOURNAL, **53**, 3114 (1931).

If the rate is first order with respect to the olefin then the integrated first order reaction rate expression is given by equation 2,

$$2.3026 \log_{10} C_0/C_t = kt \qquad (2)$$

where C_0 is the original molality of trimethylethylene, C_t is its molality at the time t (expressed in hours), and k is the specific reaction rate constant.

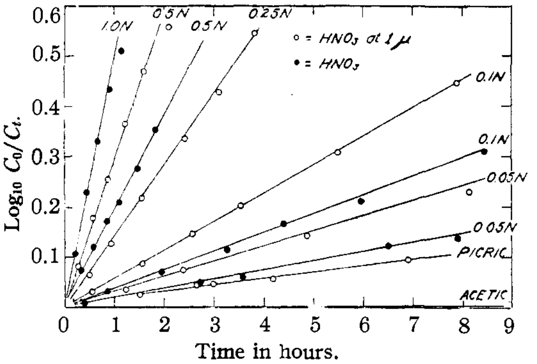

Fig. 1.—Plot of log C_0/C_t against t at 25°.

In Figs. 1, 2 and 3 are shown the plots of log C_0/C_t against t. The curves in Fig. 1 are for various strengths of nitric acid at 25° and for the weaker acids picric and acetic; those in Fig. 2 are for various other acids at 25°; and those in Fig. 3 are for nitric acid at 35°. The same scale is used in Figs. 1 and 2, but more than one origin in the latter in order to avoid crowding.

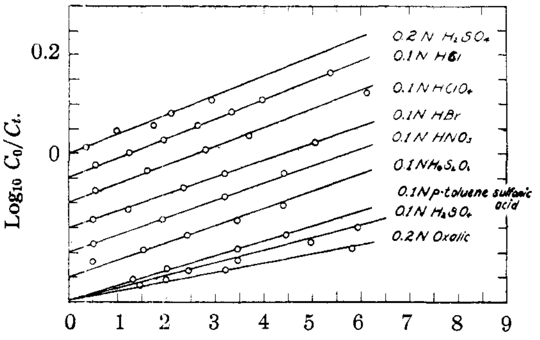

Fig. 2.—Plot of log C_0/C_t against t at 25°.

The straight line character of these curves shows that the rate is first order with respect to the concentration of trimethylethylene. As a rule these curves, after approximately 40% of the olefin had reacted, developed a curvature which indicated a decrease in the rate of disappearance of the olefin. This was probably due to the formation of a hydration resisting polymer since on standing the bromine titration value dropped to a small figure which remained constant for a long time thereafter.

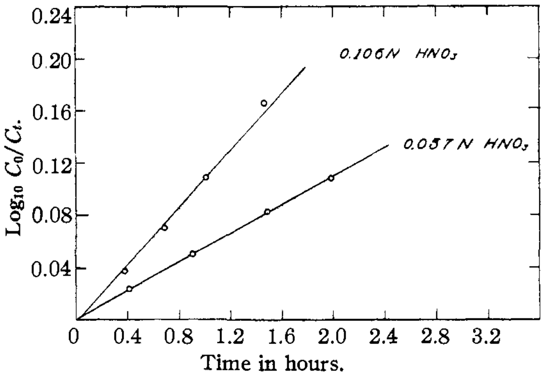

Fig. 3.—Plot of log C_0/C_t against t at 35°.

The experimental data and the values of the constants are given in Tables I and II.

TABLE I

RATE OF HYDRATION OF TRIMETHYLETHYLENE AT 25°

	Acid N	KNO_3 N	μ N	k_{25} hrs.$^{-1}$	$k\mu = k_{25}/(H_3O^+)$
HNO_3	0 0496	0.9500	1.000	0.0672	1.352
	.0990	.9008	0.999	.133	1.340
	.246	.750	.996	.324	1.316
	.515	.500	1.015	.692	1.342
	.982	....	0.982	1.255	1.278
	.516	....	.516	0.437	0.846
	.1068	....	.107	.0865	.809
	.0532	....	.053	.0410	.774
					$\frac{k_{25}}{(\text{acid}) \times 10}$
$H_2S_2O_6$	0.0932	....	0.140	0.0686	0.1474
H_2SO_4	.114	....	.087	.0560	.0982
H_2SO_4	.196	....	.133	.0905	.0923
HCl	.104	....	.104	.0943	.0905
$HClO_4$	.099	....	.099	.0845	.0854
HBr	.103	....	.103	.0865	.0840
HNO_3	.1068	....	.107	.0865	.0809
$C_7H_7SO_3H$	.0948	....	.095	.0691	.0730
Picric	.059	....	.058	.0332	.0563
Oxalic	.202	....	.100	.0418	.0414
Acetic	.105	....	.0013	.0011	.0011

The upper half of Table I gives the results obtained using nitric acid alone at concentrations of 0.05, 0.1, 0.25, 0.5 and 1 N; also using mixtures of nitric acid and sufficient potassium nitrate to give ionic strengths of 1 N. These values are in general about 60% lower than the corresponding values for isobutene, indicating that trimethylethylene hydrates at an appreciably lower rate.

When the constants obtained with nitric acid are plotted against the concentration of nitric acid, the curves shown in Fig. 4 are obtained.

From the upper curve it is evident that at constant ionic strength the rate is first order with respect to the acid. From the lower curve it is evident that the rate, at a given nitric acid concentration, is increased by the addition of potassium nitrate. This is also evident from the values of $k\mu$, $[k_{25}/(H_3O^+)]$ given in the last column of Table I. They decrease from 1.278 at an ionic strength of 0.0982 N to 0.774 at 0.532 N.

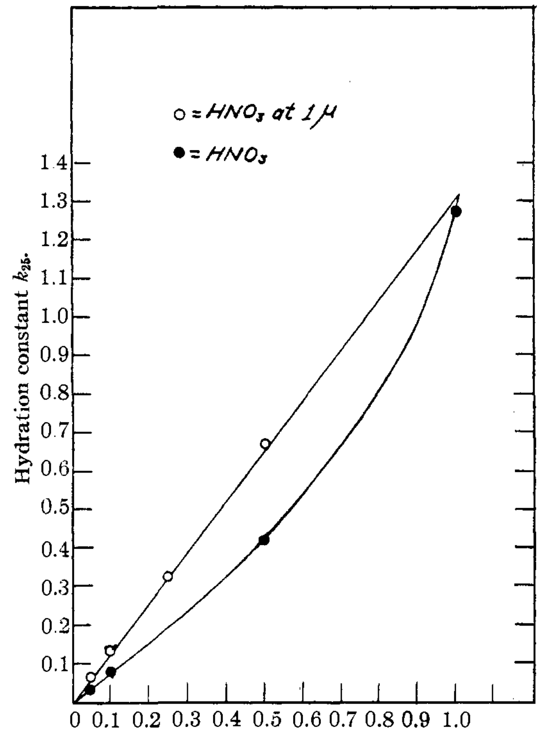

Fig. 4.—Plot of k_{25} against the concentration of nitric acid.

The lower half of Table I gives the results obtained with a variety of other acids. The concentrations were approximately 0.1 N except in the case of sulfuric, oxalic and picric acids, the first two being at 0.2 N because of the dibasic character, and the last at 0.059 N because of the low solubility. For purpose of comparison, the values were all adjusted to 0.1 M on a proportionality basis, and are shown in the last column under k_{25}/(acid) × 10. On this basis dithionic acid is the best catalyst because its second ionization, as well as the first, is strong.[8] On a 0.1 N basis, the k_{25} is 0.737, about the same as *p*-toluene sulfonic acid. Sulfuric acid, on a molal basis, is the second best catalyst, probably because its second ionization is appreciable. The best monobasic acid is hydrochloric acid.

From the hydration values at 25 and at 35°, both adjusted to the same acidity, the temperature coefficient for the ten-degree interval and the heat of activation have been calculated, Table II.

TABLE II

TEMPERATURE COEFFICIENT AND HEAT OF ACTIVATION

HNO_3 N	k_{25}	k_{35}	Temp. coefficient k_{35}/k_{25}	Heat of activation kg. cal./mole
0.100	0.0809	0.2260	2.79	18.70
.050	.0387	.1109	2.86	19.15
			2.83	18.92

The temperature coefficient, 2.83, is smaller than the corresponding value of 3.57 for isobutene,[3] and the heat of activation, 18.92 kg. cal. per mole, is likewise smaller than the value of 23.39 kg. cal. for isobutene.

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Summary

Trimethylethylene is hydrated in aqueous nitric acid to tertiary amyl alcohol. In nitric acid solutions of constant ionic strength the hydration rate is first order with respect to the concentrations of the olefin and of the nitric acid.

Many other acids hydrate this hydrocarbon at measurable rates in dilute aqueous solutions, weak acids as well as strong ones. At concentrations of 0.1 M the catalytic influence of the acids decreases in the order, dithionic, sulfuric, hydrochloric and hydrobromic, nitric, *p*-toluenesulfonic, picric, oxalic and acetic.

The temperature coefficient for the hydration rate between 25 and 35° is 2.83 and the heat of activation of the hydration reaction is 18.92 kg. cal. per mole.

PASADENA, CALIF. RECEIVED JULY 13, 1934

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[8] Ostwald, *Z. physik. Chem.*, 1, 106 (1887).