determined by means of potassium permanganate solution, distilled as follows:

Cut	B. p. at 5 mm., °C.	% by weight	$n^{20}D$
1	78- 90	12.9	1.5019
2	90- 93	31.6	1.5046
3	93- 96	28.5	1.5408
4	96-109	22.0	1.5067

Cut 2, *Anal.* Calcd. for $C_{14}H_{22}$ (dibutylbenzene): C, 88.35; H, 11.65. Found: C, 88.70; H, 11.47; d^{20}_4 0.9068; molecular refraction, 62.0.

Seven-tenths of a gram of the above-indicated Cut 2 was oxidized by heating at 165° in a sealed tube in the presence of 40 cc. of dilute nitric acid (15 cc. of 72% nitric acid and 25 cc. of water) and 0.1 g. of terephthalic acid was obtained which was identified as dimethyl terephthalate melting at 139.5–140° and showing no depression of melting point when mixed with a synthetic sample.

Fraction, 261–274° at 760 mm., $n^{20}D$ 1.5420: On selective hydrogenation at 40° in the presence of pentane as a solvent this fraction absorbed 1 mole of hydrogen per mole of hydrocarbon charged. The hydrogenated material with boiling point of 115–122° at 4 mm. and $n^{20}D$ 1.5290, analyzed as follows: *Anal.* Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74; for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.70; H, 10.28.

Complete hydrogenation of the product at 100° in the absence of solvent yielded a saturated hydrocarbon which did not react with a nitrating mixture and which analyzed as follows: *Anal.* Calcd. for $C_{14}H_{24}$: C, 87.42; H, 12.58; for $C_{14}H_{26}$: C, 86.56; H, 13.44. Found: C, 87.19; H, 12.85; $n^{20}D$ 1.4850.

These analytical results indicate that the original product consisted probably of a mixture of dicyclic and tricyclic hydrocarbons probably formed by the interaction of two moles of butadiene with one mole of benzene.

Fraction 164–180° at 5 mm. (330–352° at 760 mm.): *Anal.* Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol. wt., 264. Found: C, 90.41; H, 9.29; $n^{20}D$ 1.5635; mol. wt., 267.

Seven and three-tenths grams of this fraction was hydrogenated at 100° in the presence of a nickel–kieselguhr catalyst and at an initial hydrogen pressure of 100 atmospheres. A saturated hydrocarbon stable to a nitrating mixture was obtained boiling at 120–130° at 0.4 mm. (325–338° at 760 mm.), d^{20}_4 0.9274; and $n^{20}D$ 1.4920. *Anal.* Calcd. for $C_{20}H_{36}$: C, 86.87; H, 13.13; mol. wt., 276. Found: C, 86.63; H, 13.05; mol. wt., 266.

These analytical data show that the original product has resulted from the combination of two molecules each of benzene and butadiene in such a way as to form a tricyclic compound.

Summary

On passing a 4.5:1 molecular mixture of benzene and butadiene through a layer of silico-phosphoric acid catalyst at 216° and at 27 atmospheres pressure, 0.7 molecular proportion of benzene and all of the butadiene reacted forming a liquid product containing about 50% of phenyl-*n*-butenes and smaller amounts of 1,4-dibutenylbenzene, a dicyclic hydrocarbon formed by interaction of two molecules of butadiene with one molecule of benzene, and a tricyclic hydrocarbon formed by interaction of two molecules of butadiene with two molecules of benzene.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Kinetics of the Decomposition of Trichloroacetates in Ethyl Alcohol

BY FRANK H. VERHOEK

It has been suggested previously, in a study of the decomposition of trichloroacetates in several solvents,[1] that the rate-determining step in this decomposition is a unimolecular decomposition of the trichloroacetate ion, forming carbon dioxide and the anion of the acid chloroform, CCl_3^-. The similar hypothesis for the decomposition of trinitrobenzoates—that the trinitrobenzoate ion decomposed to carbon dioxide and the anion of the acid trinitrobenzene—was examined for the case of solutions in ethyl alcohol[2] and in mixtures of dioxane and water[3] and found to agree with the experimental facts. One of the tests of the hypothesis was made by comparing the rate of decomposition of trinitrobenzoic acid in ethyl alcohol in the presence of several aromatic amines with the basic strength of the amine. It was found that there was a quantitative relation between the number of trinitrobenzoate ions formed with amines of different strengths and the rate of decomposition. One exception to this generalization was observed, however, in the case of dimethylaniline, for which the rate of decomposition was much smaller than would be expected for the number of ions formed in the presence of a base of the strength of dimethylaniline. For the trinitrobenzoates dimethylaniline was the only tertiary amine investigated.

The present research with trichloroacetates in ethyl alcohol was undertaken to provide more quantitative data for testing the "decomposing-ion" hypothesis for the trichloroacetates, and to find out whether the behavior observed for dimethylaniline and the trinitrobenzoates was general for all tertiary amines. This paper reports the decomposition of trichloroacetic acid and its sodium salt in ethyl alcohol in the presence of primary, secondary and tertiary amines at 60 and 70°.

Experimental

The experimental measurement of the decomposition velocity was carried out in the same manner as previously,[2] with the difference that potentiometric titration was unnecessary and the titrations were made using thymol blue as indicator. It had been previously shown that hydrolysis of the chloroform formed was inappreciable in alcohol solution, and no corrections for chloride formation

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[1] Verhoek, THIS JOURNAL, **56**, 571 (1934).

[2] Verhoek, *ibid.*, **61**, 186 (1939).

[3] Trivich and Verhoek, *ibid.*, **65**, 1919 (1943).

were necessary. The solutions used were in each case 0.01 *M* in trichloroacetic acid and 0.01 *M* in amine.

Wherever possible the amine and trichloroacetic acid were added together in the form of a solid salt. These salts were usually prepared by mixing equivalent quantities of the amine and trichloroacetic acid—each purified by a distillation in the vacuum produced by an oil pump—in benzene solution, filtering off the precipitate, and recrystallizing by dissolving in ethyl acetate or absolute alcohol at room temperature and cooling in a bath of acetone and Dry Ice. The salts which did not precipitate from benzene solutions were prepared by mixing equivalent quantities of amine and acid in ethyl acetate solution, and cooling in a bath of Dry Ice and acetone. Some amines refused to form a solid salt by any of the methods tried, and for these cases—methyl-*p*-toluidine, ethyl-*o*-toluidine, dimethyl-α-naphthylamine—the solutions for study were made by mixing equivalent quantities of freshly prepared alcoholic solutions of the amine and of trichloroacetic acid and diluting to 0.01 *M*. Pyridinium, quinolinium, and dimethylanilinium trichloroacetate turn dark, liquefy, and smell of amine on standing for a few weeks.

The solvent was prepared by refluxing absolute alcohol over drierite and distilling from drierite.

Results

The mechanism of the decomposition is assumed to be

$$\mathrm{CCl_3COOH} + \mathrm{B} \overset{K}{\rightleftarrows} \mathrm{CCl_3COO^-} + \mathrm{BH^+} \quad (1)$$

$$\mathrm{CCl_3COO^-} \xrightarrow{k} \mathrm{CCl_3^-} + \mathrm{CO_2} \quad (2)$$

where K is the equilibrium constant for the protolysis reaction and k the velocity constant of the decomposition. The anion $\mathrm{CCl_3^-}$ is a strong base and quickly acquires a proton from its surroundings to form chloroform, which is the final product. As shown previously,[2] the rate of decomposition is then given by

$$-\frac{d\,[\mathrm{CCl_3COOH}]}{dt} = k\sqrt{\frac{K_{\mathrm{CCl_3COOH}}}{K_{\mathrm{BH^+}}}}\sqrt{[\mathrm{B}]}\,\sqrt{[\mathrm{CCl_3COOH}]} \quad (3)$$

As a first approximation the values of [B] and [$\mathrm{CCl_3COOH}$] substituted in (3) may be the measured stoichiometric values, as if no acid nor base had disappeared to form ions. Making this assumption the equation may be integrated with the concentration of base a constant, b, since no base is used in the reaction, giving

$$\sqrt{[\mathrm{CCl_3COOH}]} = -k'\sqrt{b}\,t + \text{constant} \quad (4)$$

where

$$k' = \frac{k}{2}\sqrt{\frac{K_{\mathrm{CCl_3COOH}}}{K_{\mathrm{BH^+}}}} \quad (5)$$

The hypothesis that the anion of trichloroacetic acid decomposes unimolecularly in the rate-determining step may then be tested by examining the form of the rate curve for a particular experiment according to (4), and by correlating the velocity constant with the strength of the base according to (5).

Equation (4) was found to be valid. In Table I are shown data for representative runs in which the time, the concentration of acid expressed in cubic centimeters of 0.01082 *N* NaOH and the function

$$\left(\sqrt{[\mathrm{CCl_3COOH}]_0} - \sqrt{[\mathrm{CCl_3COOH}]_t}\right)/t = k'\sqrt{b} = \text{constant}$$

are given.

TABLE I

TEST OF THE HALF-ORDER COURSE OF THE REACTION

t in min.	[HA]	$k'\sqrt{b} \times 10^3$
	p-Chloro-aniline at 60°	
0	9.13	
115	7.82	1.96
240	6.57	1.91
360	5.48	1.89
480	4.50	1.88
	Ethyl-*o*-toluidine at 70°	
0	8.85	
45	6.53	9.30
80	4.98	9.30
111	3.67	9.51
165	2.00	9.46
	Pyridine at 60°	
0	9.06	
96	7.64	2.57
270	5.35	2.58
390	4.05	2.56
561	2.60	2.49

The expression (5) can readily be tested by taking logarithms of both sides and plotting log k' against $-\log K_{\mathrm{BH^+}} = pK_{\mathrm{BH^+}}$; the resulting curve should be a straight line of slope one-half. The ionization constants of most of the bases in ethyl alcohol are available from the work of Goldschmidt and Mathiesen.[4] For the three secondary and one tertiary amine for which these values are not available, the dissociation constants in water[5] were converted to those in alcohol using the average values of $pK_{\mathrm{EtOH}} - pK_{\mathrm{H_2O}}$ (+0.59 for secondary amines, −0.31 for tertiary amines) found by Goldschmidt and Mathiesen. All the pK values are at 25°. The results are given in Table II and plotted in the figure. The slope to be expected from equation (5) is shown by the dotted lines.

It is evident from the figure that the predicted increase in rate with increasing basic strength is observed, but that the experimental points might better be fitted by lines of slope somewhat less than one-half. Aside from the facts that the ionization constant values in alcohol are not too certain and are being used at temperature 35° above those at which they were measured, two additional reasons may be offered in explanation of the failure of the reaction rate to keep pace with the increase in basic strength. The approximation in equation (4), that the equilibrium in equation

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[4] Goldschmidt and Mathiesen, *Z. physik. Chem.*, **119**, 439 (1926).

[5] Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

TABLE II

VARIATION IN VELOCITY CONSTANT WITH STRENGTH OF BASE

Base	pK_{BH^+}	$-\log k'_{60°}$	$-\log k'_{70°}$
o-Chloro-aniline	3.26	5.51	4.91
m-Chloro-aniline	4.21	5.22	4.69
p-Chloro-aniline	4.66	4.98	4.43
Aniline	5.70	4.63	4.07
p-Toluidine	6.27	4.52	3.94
Ethyl-α-naphthylamine	4.83[a]	5.02	4.46
Methylaniline	4.89	4.88	4.32
Ethyl-*o*-toluidine	5.51[a]	4.84	4.27
Methyl-*p*-toluidine	5.92[a]	4.63	4.05
Dimethylaniline	4.40[b]	4.89	4.31
Dimethyl-α-naphthylamine	4.57[a]	5.14	4.61
Quinoline	4.58	4.94	4.36
Pyridine	4.72	4.85	4.26

[a] Converted from pK_{BH^+} in water. [b] Goldschmidt regards this value as doubtful.

(1) is but slightly displaced to the right, becomes less valid as the strength of the base increases. With the stronger bases, the actual concentration of un-ionized acid is smaller than the measured concentration, and becomes progressively smaller as the reaction goes toward completion. This makes the value of k' smaller than it should be, and may even cause a curvature in graphs of $\sqrt{[CCl_3COOH]}$ against time. Such a curvature is observed in the experiments with aniline and *p*-toluidine, but it is hardly greater than the experimental error, and is not observed with ethyl-*o*-toluidine nor methyl-*p*-toluidine. The second reason is that it is likely that there is a salt effect in the reaction tending to make it go more slowly at higher concentrations. This has been observed for the decomposition of lithium trinitrobenzoate in alcohol.[2] With the stronger bases, the equilibrium (1) is farther on the right, there is more salt present, and the reaction proceeds less rapidly than would be predicted if the increase in ionization alone were affecting the rate.

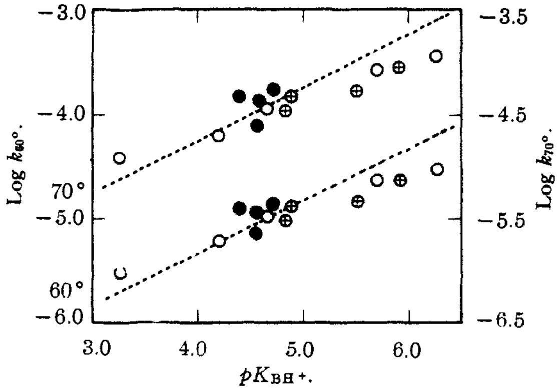

Fig. 1.—Effect of changing basic strength on the rate of decomposition of amine trichloroacetates in ethyl alcohol: open circles, primary amines; crossed circles, secondary amines; full circles, tertiary amines. The dotted lines show the slope predicted by equation (5).

The figure also shows that there are no differences in the effect of primary, secondary, and tertiary amines on the decomposition of trichloroacetates in ethyl alcohol. This suggests that the discrepancy observed for dimethylaniline in the trinitrobenzoate case[2] is due only to the erroneous postulate concerning the equality of the change in the dissociation constants of primary amines and dimethylaniline when passing from water to alcohol, based upon the work of Deyrup.[6] Deyrup's value for the dissociation constant of anilinium ion in ethyl alcohol appears to be much too large.[7] Accordingly, if a plot of log k' against Goldschmidt and Mathiesen's values for pK_{BH^+} in alcohol is prepared for the trinitrobenzoate decomposition, revising Fig. 3 of the previous paper,[2] it is found that the point for dimethylaniline lies on the curve which passes through the points for the primary amines. This graph also shows a deviation from the predicted slope (0.5) in the same direction as for the figure in the present paper, indicating again the direct correspondence between the trichloroacetate and trinitrobenzoate decompositions.

The possibility of an effect on the reaction rate due to the presence of an amine in the reaction mixture was examined by studying the decomposition of sodium trichloroacetate in the presence of aniline and of dimethylaniline. If the presence of these bases accelerated or retarded the decomposition of the ion, a difference in rate in the two cases should appear, since in the sodium salt solutions the decomposition is that of the ion and follows the first order law. It was found, however, that the decomposition of 0.01 *M* sodium trichloroacetate by itself, in the presence of 0.01668 *M* aniline and in the presence of 0.01247 *M* dimethylaniline, was in each case a first order reaction with the same velocity constant.

The average value of the temperature coefficient was 29,700 calories. This is somewhat lower than the value previously reported for ethyl alcohol,[1] obtained from experiments at higher ion concentrations.

Summary

In an investigation of the decomposition of trichloroacetic acid in the presence of various primary, secondary, and tertiary amines in ethyl alcohol at 60 and 70°, the rate variation confirms the hypothesis that the rate is determined by the concentration of trichloroacetate ion in the solution, and is unaffected by the primary, secondary, or tertiary character of the amine.

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(6) Deyrup, THIS JOURNAL, 56, 60 (1934).

(7) This makes doubtful the value for the dissociation constant of trinitrobenzoic acid in alcohol reported in the previous paper (ref. 2). Using Goldschmidt's value for the dissociation constant of anilinium ion, the dissociation constant for trinitrobenzoic acid calculated there becomes 1.8×10^{-4}, which agrees with previous work.