flask; 0.5 g. of sodium bicarbonate and 100 cc. of benzene were added and then 1.93 g. (0.0076 mole) of dithizone was added in small amounts with continuous rotation of the flask. At each addition the color became red. The flask was shaken mechanically for fourteen hours. The color remained red.

The aqueous layer was separated and acidified with acetic acid after the benzene soluble material had been removed by washing with benzene. A very light, pinkish compound was obtained from the water; m. p. 288–289°. This was identified as the disulfide of thiosalicylic acid.

The benzene layer was washed twice with 25 cc. of water and then with 15-cc. portions of 5 *N* ammonia until the aqueous layer became almost colorless. This insured the complete removal of dithizone. After a final washing with water the benzene solution was dried with calcium chloride and the product was isolated as described above except that the temperature was kept below 50°; m. p. 158–158.5°. This material was identified further spectrophotometrically as ethylmercuric dithizonate.

(b) ***m*-Tolylmercuric Thioglycolate.**—*m*-Tolylmercuric thioglycolic acid was prepared by the reaction of equimolar quantities of *m*-tolylmercuric chloride and the sodium salt of thioglycolic acid in aqueous bicarbonate solution. Upon acidification of the reaction mixture, *m*-tolylmercuric thioglycolic acid precipitated. This material was reprecipitated three times from bicarbonate solution with hydrochloric acid solution and then recrystallized several times from ethanol. White needles were obtained, m. p. 190–193° (dec.), when placed in a bath preheated to 185°.[15]

A benzene solution of dithizone was shaken with a water solution of the sodium salt of *m*-tolylmercuric thioglycolic acid. The benzene layer changed color immediately from green to orange. After separation, the water layer has a strong sulfhydryl test with nitroprusside. The nitroprusside test had been negative for the aqueous solution of the sodium salt of the mercurial before reaction with dithizone. The odor of thioglycolic acid in the water layer was unmistakable. Upon evaporation of the benzene solution, an orange solid was obtained and identified as mercury bis-dithizonate.

Spectrophotometric Identification of Dithizone Derivatives.—The method used is that of indirect solubility determination by the determination of the absorption spectrum of a saturated solution of the compound in question.[8] Comparative curves on two samples of mercuric bis-dithizonate and two of ethylmercuric dithizonate are given in Figs. 1 and 2. The method is reasonably rapid and very satisfactory for use on compounds which decompose on heating.

Summary

1. Dithizone will react with the mercury in mercurials of the types HgX_2, $R'HgX$, R'_2Hg, $R'HgSR''$, and $(R'S)_2Hg$.
2. Dithizone will cleave C–Hg bonds to form S–Hg bonds.
3. Alkyl and aryl mercuric dithizonates tested could be cleaved further to yield mercuric bis-dithizonate.
4. Mercury can exchange between different sulfur compounds.
5. Mercuric bis-dithizonate and certain other mercurial dithizonates are reversibly sensitive to light.

BALTIMORE 18, MARYLAND RECEIVED JUNE 21, 1949

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[15] See Kharasch, U. S. Patent 1,589,599 (June 22, 1926); Re 16,921, April 3, 1928; 1,672,615 (June 5, 1928).

[CONTRIBUTION NO. 68 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Rates of Ethanolysis of the Mono- and Dichloropropenes

BY HILTON A. SMITH* AND W. HOLMES KING

Introduction

Several studies of the rates of ethanolysis of chloropropenes have been published. The rates of reaction of allyl chloride and certain substituted allyl chlorides with sodium ethylate in absolute alcohol at 35 and 50° have been reported.[1] Andrews and Kepner[2] determined the rates of ethanolysis and hydrolysis of certain allyl chloride derivatives in 50% aqueous ethanol at 25°. Hatch and Alexander[3] report similar studies.

The purpose of the present work was to study the rates of ethanolysis of all of the dichloropropenes in absolute ethanol over the temperature range 25–65°, in order to compare their relative reactivities. Similar data on the monochloropropenes were also obtained.

Experimental

Dichloropropenes.—The preparation and properties of the dichloropropenes will be reported in connection with a study of their electric moments.[4] The same materials were used for rate studies.

Monochloropropenes.—The preparation and properties of the *trans*-1-chloropropene-1 (37° isomer) will also be given.[4] The *cis*-isomer was purified by refractionation of the cut distilling around 31°, obtained in the separation of the two isomers.[4] Both fractionations were carried out in an eight-foot Vigreux column.

2-Chloropropene-1 was purified by fractionation through the Vigreux column of foreshot materials obtained from the preparation of the 1-chloropropenes.[5]

Eastman Kodak Co. best grade allyl chloride was dried over anhydrous potassium carbonate, and purified by fractionation through the Vigreux column. The physical properties of the monochloropropenes are given in Table I.

TABLE I

PHYSICAL PROPERTIES OF THE MONOCHLOROPROPENES

Isomer	$n^{20}D$	Distillation temperature °C.	Distillation temperature Mm.
Allyl chloride	1.4142	44.2	737
trans-1-Chloropropene-1	1.4060	37.0	738
cis-1-Chloropropene-1	1.4060	30.8	738
2-Chloropropene-1		22.6–23.0	739

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* Harvard University Ph.D. 1934.

[1] Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[2] Andrews and Kepner, THIS JOURNAL, **70**, 3456 (1948).

[3] Hatch and Alexander, *ibid.*, **71**, 1037 (1949).

[4] King and Smith, work to be published.

[5] These foreshot materials were donated by the Columbia Organic Chemicals Company, Inc., of Columbia, South Carolina. The authors are indebted to this Company for them.

Kinetic Studies.—The quantity of the individual isomers necessary to form 100 ml. of solution 0.25 molar with respect to dichloropropene concentration was weighed into a 100-ml. volumetric flask fitted with a ground glass stopper. Into a second such flask was delivered from a buret a volume of standard solution of sodium ethoxide in absolute ethanol which would also give 100 ml. of solution 0.25 molar with respect to ethoxide ion concentration. Each solution was then diluted with such a volume of absolute ethanol that upon mixing the two solutions a total volume of 100 ml. would be obtained at the particular temperature at which rate constants were being measured, allowance being made for the thermal expansion of the alcohol.

The two flasks were then immersed in the constant temperature baths which were controlled to ±0.01° and were allowed to come to thermal equilibrium. They were then removed, the two solutions were poured together and thoroughly mixed by vigorous shaking and the flask then returned to the bath. At various time intervals a 10-ml. portion of the reaction mixture was withdrawn by means of a calibrated pipet and analyzed by immediately titrating the excess sodium ethoxide with a standard solution of hydrochloric acid in absolute ethanol, using phenolphthalein as the indicator.

Extent and Products of Reaction

For the dichloropropenes, there is the possibility that more than one chlorine might react with the ethoxide ion. Accordingly reaction of the 1,3-, 2,3-, 3,3-, and *cis*-1,2-dichloropropenes with excess ethoxide was tested. Duplicate runs were carried out in which the initial concentrations were 0.300 molar with respect to ethoxide ion and 0.100 molar with respect to dichloropropene. For the faster reacting 1,3-isomers runs were made at 55°, while for the remaining isomers a temperature of 65° was employed. Plots of $\log b(a - x)/a(b - x)$ against time were made. Here a and b denote the original concentrations of chloropropene and sodium ethoxide respectively and x denotes the concentration of each which reacts at time, t.

Rate data were taken until concentrations corresponding to better than 80% removal of a single chlorine atom had been attained. For the faster reacting 1,3- and 2,3-isomers no deviation from linearity was observed. For the slower reacting 1,2- and 3,3-isomers, slight deviations did occur after long periods of time. These were undoubtedly caused by experimental difficulties such as solvent evaporation and reaction of the alkali with the glass reaction vessels.

Rate constants obtained from the slopes of the straight-line plots agreed well with those for runs made at the same temperatures, but in which the initial concentrations of reactants were each 0.250 molar.

These same reaction mixtures were allowed to remain in the thermostats in order to test for the lability of the second chlorine atom. In all cases except the reaction with 3,3-dichloropropene-1, the reaction stopped after one equivalent of ethoxide had been consumed. For the 3,3-compound, the consumption of ethoxide was almost negligible after this point, although a slight further reaction did occur. No attempts to ascertain whether more than one equivalent of chlorine could be displaced were made with the other isomers, since their initial rates of reaction were exceedingly slow.

One would probably expect that in isomers containing a chlorine in the 3-position, this allylic chlorine would be the one to react. Thus the two 1,3 isomers would yield two isomeric 1-chloro, 3-ethoxy-propenes. In order to isolate reaction products, the following procedure was used:

Six grams of freshly cut sodium metal was dissolved in 200 ml. of absolute ethanol. Approximately 100 ml. of excess alcohol was then removed by distillation from a Claisen flask. The resulting solution was transferred to a glass stoppered bottle and 25 ml. of the dichloropropene (approximately $^1/_4$ mole) was added in small portions. Reaction of the two substances was evidenced (in the case of the more reactive of the isomers) by a warming of the reaction mixture and the immediate appearance of turbidity due to the precipitation of sodium chloride. The mixture was next transferred to the 55° constant temperature bath and allowed to remain for a length of time sufficient to insure complete reaction. It was then removed, cooled to room temperature, and approximately 250 ml. of distilled water added. Addition of the water caused a separation of the reaction mixture into two layers. The lower aqueous layer was drawn off in a separatory funnel and discarded. The upper organic layer was dried over anhydrous calcium chloride. On recovery of the reaction products by fractionation in a three-foot Vigreux still, isomers with the following characteristics were obtained: product from the 112° 1,3-dichloropropene-1, b. p. 128.0° (740 mm.), n^{25}_{D} 1.4306; product from the 104° 1,3-dichloropropene-1, b. p. 120–121° (740 mm.), n^{25}_{D} 1.4282.[6]

Further proof that the chlorine atom in the 3-position was the one undergoing reaction was found by oxidizing each of the 1-chloro-3-ethoxypropenes with neutral permanganate.[7] In each case, 2.5 to 3 g. of ethoxyacetic acid, b. p. 109° (16 mm.), n^{20}_{D} 1.4209, was isolated after the oxidation of 10 g. of the ether.

Reaction between the 2,3-dichloropropene-1 and sodium ethoxide should yield 3-ethoxy-2-chloropropene-1 if the 3-chlorine undergoes displacement. This was shown to be the case. The ether recovered by distillation in the three-foot Vigreux column exhibited the following physical properties: b. p. 110.0° (737 mm.), n^{25}_{D} 1.4211. The oxidation product obtained using neutral permanganate was ethoxyacetic acid.

Attempts to isolate the products, of reaction between 1,2-dichloropropene (93° isomer) and sodium ethoxide failed to lead to any definite conclusion as to the exact nature of the process.

Analysis of the reaction mixture by the method indicated above showed that the reaction was not clean-cut in nature, for a mixture of products was obtained. Analysis by fractional distillation in the three-foot Vigreux column yielded a small fraction of 2–3 ml. of low boiling material (b. p. 31.4–32.0° (735 mm.)) and a fraction of approximately 10 ml., b. p. 70–72°. This latter fraction is believed to be an azeotropic mixture with the ethanol employed as solvent.

The 70° fraction was found to form a white crystalline solid when treated with aqueous silver nitrate solution. This solid was explosive in nature, leaving a metallic deposit of free silver on a spatula when heated over a low flame. Analysis of the solid for the percentage of silver present gave values of 56.4 and 56.2%.

The silver salt of 3-ethoxypropyne-1 contains 56.5% Ag. Formation of this compound would require shift of the ethoxy group to the 3-position.

Experimental Calculations and Results

Whenever sufficiently rapid reaction between the chloropropene and the sodium ethoxide occurred, second order rate constants were determined from the slopes of lines obtained by plotting $1/(a - x)$ against t; $(a - x)$ represents the concentration of chloropropene or sodium ethoxide remaining at time t. These plots showed no deviation from linearity whenever the reaction was of reasonable velocity. In some of the extremely slow reactions, the deviations which appeared after several weeks of reaction were probably due to experimental difficulties such as reaction of the glass vessel with the alkali, or loss of solvent.

The specific reaction rate constants are given

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(6) 1-Chloro-3-ethoxypropene has been previously reported as having a boiling point of 120–125° (*cf.* Friedel and Silva, *Compt. rend.*, **75**, 81 (1872)).

(7) *Cf.* Andrews, THIS JOURNAL, **68**, 2584 (1946).

TABLE II

REACTION RATE CONSTANTS FOR THE ETHANOLYSIS OF THE CHLOROPROPENES

Isomer	k, Liter mole^{-1} hours^{-1} 25°	35°	45°	55°	65°	Activation energy, cal./mole
	MONOCHLOROPROPENES					
Allyl chloride	0.0674	0.226	0.655	1.81		
	.0686	.224	.653	1.77		
Av.	.0680	.225	.654	1.79		21,000
2-Chloropropene	No observed reaction after 200 hours at 45°					
cis-1-Chloropropene	No observed reaction after 200 hours at 45°					
trans-1-Chloropropene	No observed reaction after 200 hours at 45°					
	DICHLOROPROPENES					
cis-1,2-Dichloropropene-1 (93° isomer)			0.0134	0.074	0.311	
			.0142	.076	.297	
Av.			.0138	.075	.304	31,900
trans-1,2-Dichloropropene-1 (76° isomer)				.0028	.0116	
				.0034	.0137	
Av.				.0031	.0127	31,500
1,3-Dichloropropene-1 (112° isomer)	0.208	0.709	2.19	5.95		
	.212	.690	1.97	5.88		
Av.	.210	.700	2.08	5.92		21,000
1,3-Dichloropropene-1 (104° isomer)	.182	.581	1.71	4.47		
	.182	.592	1.71	4.47		
Av.	.182	.587	1.71	4.47		20,600
1,1-Dichloropropene-1				0.00056	0.0035	
				.00054	.0032	
Av.				.00055	.0034	40,600
2,3-Dichloropropene-1		.068	0.229	.615	1.72	
		.068	.229	.613	1.75	
Av.		.068	.229	.614	1.74	21,600
3,3-Dichloropropene-1			.0064	.021	0.076	
			.0065	.023	.074	
			.0065	.022	.075	26,900

in Table II, together with the energies of activation. The latter were calculated from the plots of log k against the reciprocal of absolute temperature, as shown in Fig. 1.

Discussion

The reaction of allyl chloride with sodium ethylate in absolute alcohol using 0.1097 M solutions has been previously studied by Tamele, Ott, Marple and Hearne.[1] These authors find rate constants of 0.246 and 1.194 at 35 and 50°. The corresponding figures reported here are 0.225 and 1.04. The differences in the two figures may be due to differences in concentrations of reactants. Andrews and Kepner[2] found that the concentration of reactants did have such an influence. A comparison of the results of these latter authors at 25° for allyl chloride, 3,3-dichloropropene and the two geometrical isomers of 1,3-dichloropropene show findings which are in substantial agreement with those reported here.

An examination of Table II brings out several interesting observations. Of the compounds with an allylic chlorine, all except 3,3-dichloropropene-1 react with much the same velocity, and have activation energies which are not very different. Substitution of an additional chlorine in the 1-position causes a somewhat faster reaction, while substitution in the 2-position causes retardation. Substitution of an additional chlorine in the 3-position results in a rate which is only one per cent. of that of allyl chloride, with an accompanying increase in activation energy of about 6,000 calories per mole. This is so in spite of the fact that both chlorine atoms are in the allylic position.

The difference in rates of ethanolysis of the 1,3-dichloropropenes is not very large. This is a rather significant finding when taken in connection with the dipole moments of these molecules. The angle between the two chlorine vectors is always 109° in the *trans* isomer, no matter what position the 3-chlorine assumes. For the *cis* isomer, the angle between the chlorine vectors can be greater only in case the molecule exists with the two chlorine atoms as far apart as possible. In this position, the chlorine in the 1-position would appear to block completely the 3-carbon atom from attack on the face opposite the chlorine atom, yet the second order kinetic characteristics of the reaction lead to the belief that the attack is on this position. If, on the other hand, the angle between the two chlorine vectors is less than the tetrahedral angle (which would be consistent with the dipole moments if

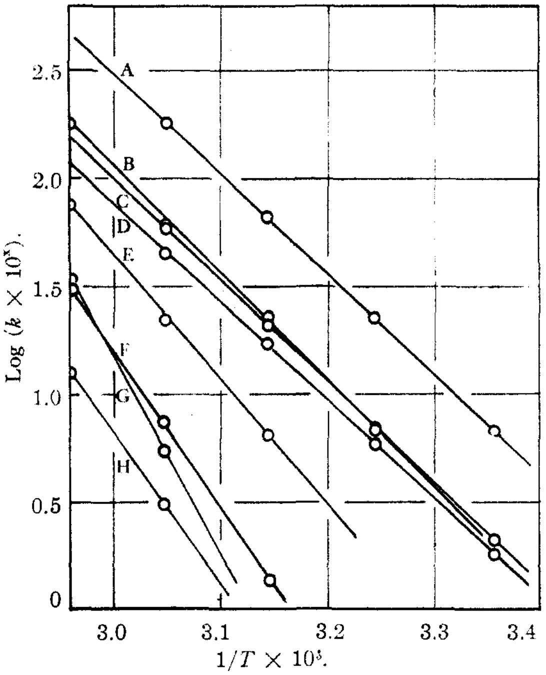

Fig. 1.—Temperature coefficients for sodium ethoxide reaction with chloropropenes in absolute EtOH: A, allyl chloride, $x = 2$; B, 2,3-dichloropropene, $x = 2$; C, 1,3-dichloropropene, 112° isomer, $x = 1$; D, 1,3-dichloropropene, 104° isomer, $x = 1$; E, 3,3-dichloropropene, $x = 3$; F, 1,2-dichloropropene, 93° isomer, $x = 2$; G, 1,1-dichloropropene, $x = 4$; H, 1,2-dichloropropene, 76° isomer, $x = 3$.

the *trans* configuration were assigned to the 112° isomer) the 1-chlorine would not interfere with the attack of the ethoxide ion on the 3-carbon.

Hatch, Gordon and Russ[8] have studied the relative rates of reaction of the two isomers of 1,3-dichloropropene with potassium iodide. They find that the rate at which the low-boiling isomer reacts with the iodide ion is approximately four times as great as the rate found when the high-boiling isomer is used.[9] This is quite different from the almost equal reactivities found here for these isomers with sodium ethoxide (see also Hatch and Alexander, ref. 3).

Since completion of the studies reported here, evidence has been presented in a Communication to the Editor by Hatch and Perry[10] which shows rather conclusively that the low-boiling isomer is actually the *cis* form.

The isomeric 1,2-dichloropropenes show very interesting results, in that the activation energies for their reaction with sodium ethoxide are the same, although the *trans* isomer reacts much more slowly than does the *cis*. If the initial reaction depends on halogen displacement, this could be explained on the basis of the fact that each chlorine atom in the *trans* configuration tends to hinder such an attack by the negatively charged ethoxide ion. If, on the other hand, the reaction is one involving dehydrochlorination, the mechanism suggested by Cristol[11] gives an equally good explanation, and is probably to be preferred.

If the principal product isolated after the reaction is 3-ethoxypropyne-1, as is suggested earlier, neither mechanism gives a satisfactory explanation for this result. It would appear that the original product must undergo further change. This presumably takes place in the recovery process, since in the original reaction only one mole of sodium ethoxide was used per mole of dichloropropene. Unfortunately, it is not clear whether the 1 or the 2-chlorine is involved in the original reaction.

It is interesting that the *cis*-1,2 compound showed as fast reaction as was found, in view of the fact that neither the 1-chloropropene or 2-chloropropene showed any reaction with sodium ethoxide after more than two hundred hours at 45°.

The very slow reaction of the 1,1-dichloropropene-1 together with its high activation energy indicate the difficulty of displacement of a chlorine atom in this position.

Summary

The rates of the reaction of sodium ethoxide with all of the isomeric mono- and di-chloropropenes have been determined in absolute ethanol. The 1-chloro- and 2-chloropropenes failed to react at a temperature of 45°. Rate constants and activation energies have been tabulated for allyl chloride and all of the dichloropropenes.

It has been shown that substitution of a chlorine in the 1-position of allyl chloride increases its rate of reaction while substitution of a chlorine in the 2 or 3 positions causes a decrease. Little difference in reactivity was found in the *cis*- and *trans*-1,3-isomers. However, for the 1,2-isomers, the *trans* compound reacts much more slowly than does the *cis*. 1,1-Dichloropropene-1 reacts the most slowly of all of the di-substituted propenes.

The reasons for the behavior of these isomers have been discussed.

KNOXVILLE, TENNESSEE RECEIVED MARCH 7, 1949

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[8] Hatch, Gordon, and Russ, THIS JOURNAL, **70**, 1003 (1948).

[9] It should be noted that the rate constants tabulated by these authors must be multiplied by 2.303 to give the specific reaction rate constants. This is also true for the rate constants for this same reaction given by Tamele and co-workers, ref. 1.

[10] Hatch and Perry, THIS JOURNAL, **71**, 3262 (1949).

[11] Cristol, THIS JOURNAL, **69**, 338 (1947); *cf.* Andrews and Kepner, *ibid.*, **69**, 2230 (1947).