[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Decomposition of Secondary Alkyl Chlorosulfites. III. The Elimination Reaction and Isotope Effects[1]

BY CHARLES E. BOOZER[2] AND EDWARD S. LEWIS

RECEIVED AUGUST 10, 1953

The decomposition of 2-pentyl chlorosulfite extensively deuterated in the 1- and 3-positions has been studied both kinetically and with regard to yields of 2-chloropentane and 2-pentene. Compared to the undeuterated compound, the rate of disappearance of chlorosulfite is slower by a factor of about 1.4 in dioxane solution and about 3.3 in isoöctane solution. In dioxane, the yields of 2-chloropentane and 2-pentene are uninfluenced by the presence of deuterium. It is concluded that the elimination and substitution reactions both go by way of a solvated carbonium ion intermediate. The rate retardation by deuterium results from hyperconjugation in the transition state. A novel polarimetric analysis for 2-chloropentane is described.

Introduction

The previous studies on the decomposition of chlorosulfites[3,4] have been concerned with the mechanism of the formation of alkyl chloride. However, from the preparative point of view, the uncatalyzed reaction of thionyl chloride with secondary alcohols is not a very good route to alkyl chlorides since olefin is produced in considerable quantity. Thus the yield of olefin from the decomposition of 2-pentyl chlorosulfite is over 40%[3] and cyclohexene can be produced in over 80% yield from cyclohexyl chlorosulfite.[5] It therefore seemed of interest to study the elimination reaction. An approach to this study was the investigation of rates and yields in the decomposition of 2-pentyl chlorosulfite with deuterium substituted in the 1- and 3-positions. On the assumption that a rate-determining step involving breakage of the carbon–hydrogen bond would produce a retardation in rate comparable to those previously observed for reaction showing such a bond breakage,[6-8] and assuming that no retardation would occur if this bond were not broken,[9] there appeared to be a simple test of the sequence of any steps that might take place. The only previously reported cases of isotope effects on rates where the bonds were not broken have been very small effects observed in the oxidation of isopropyl alcohol[8] and the displacement of bromide accompanying the elimination in the reaction of isopropyl bromide with ethoxide.[6]

Experimental

Materials.—Matheson best grade pentanone-2 was purified by distillation through an efficient packed column; it boiled at 101.8–102.0 with $n^{20}\mathrm{D}$ 1.3901. Pentanol-2, butanol-2, dioxane and the chlorosulfites were prepared and purified as before.[4]

Preparation of Deuterated Alcohol.—The deuterated pentanol-2 was prepared by exchange of 99.8% deuterium oxide with pentanone-2 followed by reduction with lithium aluminum hydride. The procedure was essentially the same as that used by Shiner.[6] Five samples of pentanone-2 weighing 22 g. each were placed in a row of five flasks equipped with reflux condensers. A 10-g. sample of 99.8% deuterium oxide containing 0.1 g. of potassium carbonate was exchanged with the first ketone sample. The mixture was refluxed for 16 hours, cooled, and the deuterium oxide transferred to the next flask with a pipet. The process was repeated until the deuterium oxide had been exchanged with all five ketone samples. After the five exchanges, the ketone dissolved in the spent deuterium oxide was removed by distillation and returned to the flask containing the last ketone sample. The per cent. deuterium oxide in this sample of water was estimated after each exchange from the refractive index of a distilled sample.[10] Starting with the first exchange the values were 52, 21, 12, 6 and 3% deuterium, respectively. A second 99.8% deuterium oxide sample, exchanged in order with each of the ketone samples in the same manner as the first, had 78, 55, 35, 20 and 10% deuterium oxide after the exchanges. Two more fresh deuterium oxide samples were similarly exchanged down the line of ketone samples but their composition was determined only after the five exchanges. They contained 19 and 33% deuterium oxide, respectively, after these exchanges. After two more fresh deuterium oxide samples had gone through the line, four more samples were used but this time each sample was started one flask further down the line so that the final exchange for each ketone sample was with fresh deuterium oxide. The excess water was removed by azeotropic distillation from the combined ketone samples, and the ketone was dried over "Drierite." The deuterated pentanone-2, 100 g., b.p. 101.9–102.0° (uncor.), was reduced with a slight excess of lithium aluminum hydride in ether to produce 95 g. of deuterated pentanol-2, b.p. 118.0–118.5° (uncor.).

Analysis for Deuterium.—The extent of deuteration was determined by density measurements on the water produced from combustion of the ketone and alcohol.[11]

A micropipet was constructed from 0.5 mm. bore Pyrex capillary tubing for use as a pycnometer. It contained about 50 microliters. The tip was made very fine to reduce loss by evaporation. Instead of the usual etched calibration mark, a fine capillary constriction was made at the desired position. The mid-point of this capillary was taken as the mark, and since it was very fine, the setting was accurate and easy to make. The pycnometer was filled at 25.00°, weighed on a microbalance, and the deuterium oxide content was calculated from a table of relative densities *versus* composition.[11] The accuracy of this method is limited by the small samples of water weighed. Loss due to evaporation and difficulty with electrostatic charges made it difficult to weigh the samples to closer than 0.02 mg. which corresponds to 0.004 in density or 0.4% deuterium oxide in the water. The error in the percentage of the possible hydrogens replaced is about 1%. For the ketone and alcohol, respectively, it was found that 87 and 86% of the replaceable hydrogens had been replaced. This analysis corresponds to 4.3 atoms of deuterium per mole of alcohol.

Kinetic Methods.—The disappearance of chlorosulfite was followed spectrophotometrically as before.[3] Concentrations of about 0.05 *M* chlorosulfite were usually used. The samples were taken with a 0.05-ml. micropipet and diluted with 10.0 ml. of isoöctane before measuring the optical density at 234 mμ. After correcting for residual ab-

---

(1) This paper includes the results previously published in preliminary form, E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 6306 (1952).

(2) Ethyl Corporation Fellow, 1952–1953.

(3) E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 308 (1952).

(4) C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953).

(5) T. C. Singleton, unpublished observations.

(6) V. J. Shiner, Jr., THIS JOURNAL, **74**, 5285 (1952).

(7) W. F. K. Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934).

(8) M. Cohen and F. H. Westheimer, THIS JOURNAL, **74**, 4387 (1952).

(9) L. Melander, *Archiv. Kemi*, **2**, 211 (1950).

(10) D. B. Luten, Jr., *Phys. Rev.*, **45**, 161 (1934).

(11) W. E. Siri, "Isotopic Tracers and Nuclear Radiations," McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

sorption, the optical densities were used to calculate the first-order rate constants k both from the equation $\log d = (k/2.303)t + c$ and the equation $\log \Delta d = (k/2.303)t + c$ where t is the time in seconds, d the optical density, and Δd the change in optical density for a constant time interval.[12] The rate constants were calculated from the slopes of the lines estimated visually to be the best fit to the points of the plot of $\log d$ or $\log \Delta d$ against t and also from the above equation using the method of least squares to find the best line. The reactions were usually followed to within 80 to 90% of completion, giving about 8 analytical points in the range of 1.000 to 0.100 on the optical density scale. All points were weighed equally in the calculations. In one run at 77.5°, a visually drawn line for the first equation above gave $k = 9.19 \times 10^{-4}$/sec., the least square treatment of the same data gave $k = 9.08 \times 10^{-4}$, a visually drawn line for the second plot by the Guggenheim method gave $k = 9.45 \times 10^{-4}$ and the least squares calculation for this method gave $k = 9.31 \times 10^{-4}$. The variations of these results from the average and the variation of duplicate runs are the basis of the estimations of error in Table I.

Product Analysis.—In order to determine the ratio of alkyl chloride to olefin produced from the decomposition of 2-alkyl chlorosulfite in dioxane, a new analytical method was developed. The method is based on the fact that the optical rotation of a substance is proportional to the concentration of optically active material in that substance. A weighed sample, about 1 g., of alkyl chloride of known activity was added to the dioxane solution containing the unknown quantity of inactive chloride, usually about 2 g. Some pure alkyl chloride was isolated from this mixture as previously described,[4] and the optical rotation measured carefully. The green mercury line was used throughout these determinations because the rotations are larger and the observation is easier and more accurate than with the D-line. From the weight of original chloride, the original rotation and the rotation after dilution, the weight of chloride in the solution was calculated. The observed rotation of the original chloride was about 5° and the diluted chloride 2°. The rotations were measured to within 0.01° giving a final accuracy of 1% or better in the per cent. yield of alkyl chloride. A method of estimating the olefin produced was to titrate the hydrogen chloride evolved during the decomposition of the alkyl chlorosulfite. These two methods usually accounted for 99–100% of the chlorine in the original chlorosulfite, but the hydrogen chloride evolution was unexpectedly slow and therefore not always carried to completion; for this reason it was not very reproducible.

Pentene-2, b.p. 36.0–36.5° (uncor.), was isolated by distillation from the chlorosulfite decomposition mixtures in quantities roughly corresponding to the hydrogen chloride yields. The pentene-2 produced from the deuterated chlorosulfite was analyzed for deuterium by the method used on the original alcohol. Values of 84 and 86% from two determinations gave an average of 85% of the hydrogen in the 1- and 3-positions substituted by deuterium.

Discussion

Table I shows the rates of decomposition of the deuterated and undeuterated 2-pentyl chlorosulfites, and Table II shows the yields of alkyl chloride and in some cases hydrogen chloride for the same compounds under similar conditions, and also the yields of the corresponding products from 2-butyl chlorosulfite. The yields of HCl from the deuterated 2-pentyl compound are not given, since the lower reaction rate was not allowed for in collecting it.

The estimated errors in Table II are based on the deviations of duplicate runs from the average. It can be seen from this table that the previously reported difference in yields of alkyl chloride from the two chlorosulfites was largely an artifact of the isolation procedure.

TABLE I

RATES OF DECOMPOSITION OF 2-PENTYL CHLOROSULFITE

Substituents	Solvent	Temp., °C.	$k \times 10^4$, sec.$^{-1}$
H	Dioxane	61.5	2.18 ± 0.02
D	Dioxane	61.5	1.48 ± .05
H	Dioxane	77.5	9.3 ± .2
D	Dioxane	77.5	6.6 ± .2
H	Isoöctane	95.5	0.167 ± .002
D	Isoöctane	95.5	0.050 ± .001

TABLE II

PRODUCTS OF DECOMPOSITION OF *s*-ALKYL CHLOROSULFITES IN DIOXANE

Compd.	Temp., °C.	RCl, %	HCl, %
2-Butyl	61.5	52.1 ± 0.7	49.4 ± 0.4
2-Butyl	77.5	45.5 ± .5	54.6 ± .4
2-Pentyl	61.5	51.0 ± .5	48.8 ± .8
Deuterated 2-pentyl	61.5	51.2 ± .3	
2-Pentyl	77.5	44.3 ± .4	
Deuterated 2-pentyl	77.5	46.6	

Table I shows that the substitution of deuterium for hydrogen resulted in a significant retardation of the over-all rate, but the nearly unaltered yields of alkyl chloride shows that the rate of formation of alkyl chloride must be retarded just as much as that of the olefin. The most obvious conclusion to be drawn from this is that there is a common rate-determining step, which is retarded by the presence of deuterium. One can also conclude that the subsequent steps, one of which gives alkyl chloride and the other olefin from this common intermediate are not differently influenced by the deuterium substitution. The fact that deuterium substitution has almost no effect on the rate of the olefin-forming step is also shown by the observation that virtually no isotopic fractionation occurs in the elimination process, since the starting alcohol has 86% of the 1- and 3-positions occupied by deuterium and 85% of the same positions on the olefin are deuterated.

The previously proposed mechanisms for chlorosulfite decompositions are consistent with these observations. If the intermediate is indeed a solvated carbonium ion, it is reasonable that hyperconjugation will draw electrons from the bonds to the β-hydrogens to the electron deficient carbon, reducing the force constants of the C–H bonds. This .reduction in force constant gives rise to a greater reduction in zero point energy on going from the protium compound to its transition state than will be found for the deuterium compound, thus the heat of activation of the deuterated compound will be higher. A more complete discussion of this effect on this and other ionization reactions is to be found in the accompanying paper.[13]

In isoöctane the rate retardation is much greater; this is consistent with the previously stated view[4] that this solvent can in no way participate in the ionization; thus the electron deficiency is higher and the hyperconjugation more important than it is in the case of the dioxane solvent, where the nucleophilic nature of the solvent assists the ionization and reduces the electron deficiency.

The lack of retardation by deuterium on going from the solvated carbonium ion to the olefin (shown both by the unaltered yield and the lack

---

[12] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

[13] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **76**, 791 (1954).

of isotopic fractionation) requires comment, since usually bond-breaking reactions will show an isotope effect. It seems likely that this step does indeed require activation energy, since the relative yields of olefin and alkyl halide are temperature sensitive, suggesting that the elimination process has an activation energy about 780 cal. higher than the displacement process. The consequence of this observation is that the sum of the zero point energies of vibration of the carbon–hydrogen bonds must be unchanged on going from the carbonium ion to the transition state. Two explanations can be offered for this lack of detectable isotope effect. In the first, consideration may be given not only to the bond which is being broken, but to all the other bonds as well. Thus if the weakening of all 5 bonds to β-hydrogens were the same, a reduction in the zero point energy of one of these to zero might be compensated by an increase in the zero point energy of the other four, and this compensation could be exact if the force constants in the carbonium ion were only 64% of those in the second transition state. The second explanation is based on the assumption that the force constant of the bond to be broken is not much reduced in the transition state going to the olefin. This implies that the small activation energy arises from some other source than the process of breaking this bond. It is probably not necessary to look for an explanation predicting an identically zero isotope effect; we are more inclined to believe that an effect may be present, but is in this case very small.

Thus the unexpected results with the deuterium compound confirm the carbonium ion nature of the reaction and the participation of the solvent dioxane; furthermore, the elimination reaction also goes by way of the same carbonium ion.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

The Decomposition of Secondary Alkyl Chlorosulfites. IV. The Tertiary Amine Catalysis[1]

BY EDWARD S. LEWIS AND GALVIN M. COPPINGER

RECEIVED AUGUST 10, 1953

The decomposition of secondary alkyl chlorosulfites is catalyzed by tertiary amines and their hydrochlorides. A kinetic study of the reaction of isopropyl chlorosulfite in dioxane solution shows that the reaction follows a first-order course, with the apparent first-order rate constants increasing linearly with the concentration of catalyst. A bimolecular displacement of the S_N2 type between chloride ion and the chlorosulfite is proposed, which is consistent with the kinetics, the stereochemical result, the order of efficacies of the various catalysts and the magnitude of rate retardation with deuterium substitution in the β-positions. In the case of catalysis by the free amines, chloride ion is believed to arise from a prior elimination reaction. A positive salt effect is present, but is not alone responsible for the increase in rate on adding amine hydrochlorides.

Introduction

There are several examples of the profound effect of pyridine on the steric course of the reaction of alcohols with thionyl chloride.[2-4] Gerrard has attributed this effect to a catalysis of the decomposition of chlorosulfite by pyridine hydrochloride, which he was able to observe in a heterogeneous system.[5] It has also been shown that dilute solutions of pyridine hydrochloride in dioxane gave from secondary alkyl chlorosulfites an extensively inverted alkyl chloride, although configuration is retained in the absence of this salt.[6]

The studies here reported were designed to clarify the function of the base in this catalyzed decomposition. The experiments were carried out in dioxane solution since the change in stereochemical result in this solvent on adding the amine provides an additional criterion for the detection of catalysis. In most of the experiments, however, isopropyl chlorosulfite was used, because it is the most readily distillable secondary chlorosulfite, and because it was hoped that elimination would account for a smaller fraction of the product than in the other cases where a disubstituted ethylene could be produced.

Experimental

Materials.—Dioxane was boiled under reflux with sodium metal for 24 hours and distilled through a packed column. The fraction collected boiled at 101 ± 0.5° and was further purified by partial freezing, the frozen material only was used. This fractional freezing was repeated if necessary. Purity was estimated by measurement of the optical density compared to air at 230 mμ. The average optical density was 0.350, the extreme values were 0.200 and 0.450.

The tertiary bases were commercial products purified by distillation. Pyridine hydrochloride was prepared *in situ* by mixing dioxane solutions of pyridine with the calculated amount of a solution of hydrogen chloride in dioxane, standardized by titration.

Methylpyridinium chloride was prepared from the iodide by treatment with an aqueous silver chloride suspension. The iodide was prepared in the usual manner from pyridine and methyl iodide. Propylpyridinium chloride was prepared from pyridine and *n*-propyl chloride by heating in a closed flask. Both salts were recrystallized from a propyl ether–propyl alcohol mixture.

Lithium perchlorate was prepared from lithium carbonate and 70% perchloric acid. After removing the water under vacuum, the resulting trihydrate was recrystallized from ethanol. The trihydrate was dehydrated by heating at 100° and 0.5 mm. pressure for one hour.

The preparation of the chlorosulfite followed the previously described methods,[6] using alcohols prepared in the same work.[6,7] Isopropyl alcohol was purified by distillation; it gave a chlorosulfite boiling at 39–40° at 20 mm.

---

[1] Presented in part at the Los Angeles Meeting of the American Chemical Society, March, 1953.

[2] J. Kenyon, A. G. Lipscomb and H. Phillips, *J. Chem. Soc.*, 415 (1950).

[3] J. Kenyon, H. Phillips and F. M. H. Taylor. *ibid.*, 382 (1931).

[4] H. C. Stevens and O. Grummitt, THIS JOURNAL, **74**, 4876 (1952).

[5] W. Gerrard, *J. Chem. Soc.*, 99 (1949).

[6] C. E. Boozer and E. S. Lewis, THIS JOURNAL, **75**, 3182 (1953).

[7] C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954).