[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM M. RICE UNIVERSITY, HOUSTON, TEX.]

The Decomposition of Gaseous Chloroformates. II. Substitution and Elimination Stereochemistry[1]

By EDWARD S. LEWIS, WILLIAM C. HERNDON AND DONALD C. DUFFEY

The gas phase decomposition of optically active 2-butyl chloroformate yields 2-chlorobutane with clean retention of configuration. *erythro-* and *threo*-2-butyl-3-d_1 chloroformates yield 1-butene-d_1 and *cis-* and *trans*-butene-2 containing deuterium to an extent consistent with completely stereospecific *cis* elimination. The significance of some small isotope effects is discussed.

Introduction

Part I of this series[2] presented the stereochemical and kinetic background leading to the proposal of an SNi mechanism for chloroformate ester decompositions, and new kinetic measurements showed that the kinetics in the gas phase would fit with certain modifications. A complete justification for the SNi mechanism for the formation of alkyl chlorides from chloroformates also demands retention of configuration in the gas phase as well as in the liquid phase where it has already been demonstrated.[3] Since olefin is also produced from chloroformate esters,[2,4] the stereochemistry of this elimination is also of interest. The entropy of activation for elimination of about zero[2] does not suggest a rigid cyclic transition state, although in the pyrolytic elimination from xanthate esters, which has been presumed to pass through a cyclic transition state, the entropy of activation is only about −5 e.u.[5]

The early studies of elimination stereochemistry were concerned with cyclic systems which yielded only *cis*-olefins.[6] Using an open chain system leading only to *trans*-stilbene, Curtin and Kellom determined the stereochemical course of the elimination of HX from 1-X-1,2-diphenylethane-2-d_1 of known stereochemistry by observing the loss (or retention) of the deuterium.[7] In a logically similar study, the structures of the stereoisomeric 3-deuterio-2-bromobutanes were determined by a deuterium analysis of the isomeric 2-butenes resulting from the alkaline dehydrohalogenation, the stereochemical course of which is known.[8]

In this paper the argument is reversed and the course of elimination is deduced from the deuterium content of the product olefins and the known stereochemistry of the 3-deuterio-2-butyl chloroformates.

Results and Discussion

Butanol-2 of large but not maximum rotation was converted to the chloroformate, without attack on the asymmetric center; this compound, on extensive decomposition in a flow system,[2] gave a gas

(1) Presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., 1958. From portions of the 1958 Ph.D. thesis of W. C. Herndon and the 1955 M.A. thesis of Donald C. Duffey.

(2) E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

(3) A. H. J. Houssa and H. Phillips, *J. Chem. Soc.*, 108 (1932); 1232 (1932); K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

(4) A. R. Choppin and E. L. Compere, *ibid.*, **70**, 3797 (1948).

(5) G. L. O'Connor and H. R. Nace, *ibid.*, **74**, 5454 (1952).

(6) W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 198 (1940).

(7) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

(8) P. S. Skell and R. C. Allen, *ibid.*, **81**, 5383 (1959).

containing 2-chlorobutane, which was trapped, and the butyl chloride was purified and the rotation measured. The rotations of the optically pure chloride and alcohol are known,[9] so the stereochemical course can be calculated. From the measured rotations and the optical purity of the starting material, it was calculated that from optically pure alcohol, $[\alpha]^{25}D$ 13.64°, a chloride with a rotation $[\alpha]^{25}D$ 34.8° would have resulted, of the same sign and configuration as the alcohol. Optically pure 2-chlorobutane is reported to have $[\alpha]^{25}D$ 33.8°.[9] The multiplication of errors in our work resulting from the multiple dilutions makes the difference between these values of little significance, but it is clear that the extent of retention of configuration is as high as in any known reaction.

The reduction with lithium aluminum deuteride of 2,3-epoxybutane yielded 2-butanol-3-d_1. The *cis*-oxide gave the *threo* isomer, the *trans*-oxide gave the *erythro* isomer, both on the basis of the well established assumption of inversion in the ring-opening reaction. The chloroformates were prepared in the usual way and decomposed in the flow system. The deuterium contents of the resulting olefins are shown in Table I, as determined by mass spectrometry of the chromatographically separated olefins. The precision is not as high as might be possible, since the olefin separation was incomplete.[10]
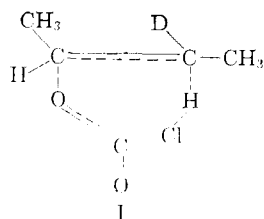
TABLE I

DEUTERIUM CONTENT OF OLEFINS FROM DECOMPOSITION OF 2-BUTYL-3-d_1 CHLOROFORMATE IN THE GAS PHASE

Compound	1-Butene, atoms D	*trans*-Butene-2, atoms D	*cis*-Butene-2, atoms D
erythro	1.01 ± 0.02	1.01 ± 0.02	0.07 ± 0.05
threo	1.06 ± 0.02	0.01 ± 0.02	1.00 ± 0.03

The structure I is a reasonable conformation of a transition state for the elimination of hydrogen chloride and carbon dioxide from *erythro*-2-butyl-3-d_1 chloroformate to yield *trans*-butene-2, and illustrates the retention of deuterium in this reaction. Table I shows that this reaction course is indeed followed for both stereoisomers and both 2-butenes. Within experimental error, the presence of any *trans* or non-specific elimination course can be excluded.

(9) R. L. Letsinger, L. G. Maury and R. L. Burwell, *ibid.*, **73**, 2373 (1951).

(10) In this case the error is not serious, but our earlier attempts using a distillation separation and a more difficult deuterium analysis made it difficult to draw even qualitative conclusions on the stereochemistry of elimination from chlorosulfites; D. C. Duffey, M.A. Thesis, The Rice Institute, 1955.

I

Decomposition rates were measured under conditions closely simulating those designed to show the stereochemical course. The rates measured, by the previously described method,[2] are given in Table II, along with similarly measured rates for the deuterium free compound from reference 2 and for 2-butyl-1-d_3 chloroformate. The notation is that of reference 2, where 1 denotes the 1-olefin, t and c denote trans- and cis-2-olefin and s denotes the substitution process. All rates are at 255°, and are in units of 10^{-5} sec.$^{-1}$. Errors are standard deviations from the numbers of runs given parenthetically after Σk_i.

TABLE II

ISOTOPE EFFECTS ON DECOMPOSITION OF 2-BUTYL CHLORO-
FORMATE

Compound	k_1	k_t	k_c	k_s	Σk_i
No D	154	147	141	761	1203 ± 36(6)
erythro-3-d_1	185	120	97.7	748	1151 ± 6(4)
threo-3-d_1	183	110	115	751	1159 ± 4(5)
1-d_3	52.3	138	134	706	1031 ± 5(3)

Isotope effects may be described as belonging to two types: primary, in which the bond to the deuterium is broken, and secondary, in which it is not. The largest effects are the primary effects, which show up in k_c in the second row (k_H/k_D = 1.44), k_t in the third row (k_H/k_D = 1.34) and k_1 in the last row (k_H/k_D = 2.91), but this last also includes a secondary effect due to the two remaining deuterium atoms. All the effects on k_s are of course secondary effects and the remaining effects on k_1, k_t and k_c are also secondary effects, and are fairly small. Of particular interest is the increase in k_1 on deuterium substitution in the 3-position (k_H/k_D = 0.83 for the erythro compound, 0.84 for the threo compound). Inverse isotope effects have been observed before and attributed in several cases to crowded transition states,[11] or to inductive effects or changes in bonding or hyperconjugation,[12] none of which appear applicable to an effect of this magnitude at this temperature. An alternative explanation is mechanistically very interesting. If there is an intermediate X common to the formation of all three butenes (for example an ion pair) and the formation of one of the butenes from X is substantially retarded by a primary isotope effect, that of another is slightly retarded by a secondary effect, and that of the third is insensitive to the substitution, then the steady state concentration of X will be increased by deuterium substitution and

the over-all rate of the third reaction (1-butene formation) can increase, to an extent less than the decrease in rates of formation of the 2-butenes. The precision in the determination of the isotope effects does not justify a quantitative explanation or any attempt to explain the apparent lack of this effect in the reactions of 2-butyl-1-d_3 chloroformate. We may regard these isotope effects as strong but insufficient evidence for an intermediate in the elimination reaction.

The secondary isotope effect on k_s is small. In terms of free energy of activation ($\Delta F_D^* - \Delta F_H^*$), deuterium in the 3-position contributes about 16 cal., and each deuterium in the 1-position contributes about 26 cal., probably not experimentally distinct. If we assume that this free energy difference would be the same in the neighborhood of room temperature, then the effect of β-deuterium is less than in that in solvolytic reactions or chlorosulfite decompositions in solution,[13] suggesting a transition state less electron deficient than that of reactions leading to familiar carbonium ions. The danger of this temperature extrapolation has been pointed out by Shiner.[14]

In sum, the stereochemistry of both elimination and substitution is consistent with a cyclic transition state or intermediate, six-membered for the elimination, four-membered for substitution. The isotope effects suggest but do not require an intermediate in the elimination reaction, and transition states with appreciably but not conspicuously electron deficient carbon.

Experimental

erythro-2-Butanol-3-d_1.—Lithium aluminum deuteride (7.5 g., 0.178 mole) was placed in a 500-ml. 3-neck flask, covered with 125 ml. of anhydrous ether, and the solvent was boiled under reflux for 2 hours. The resulting suspension was cooled, then 51.4 g. (0.712 mole) of trans-2,3-epoxybutane (prepared from 99% trans-2-butene by the procedure of Lucas and Pressman[15]) was added at a rate sufficient to cause moderate boiling; it was complete in about 2 hours. Boiling was continued for 18–24 more hours, then moist ether (25 ml.) was added, and then water. The reaction mixture was shaken with 200 ml. of 15% aqueous potassium hydroxide, the phases were separated, the aqueous phase extracted twice with 50-ml. portions of ether, and most of the ether removed by distillation. The residue was dried with calcium oxide, which also removed unreacted epoxide, and then distilled through a center rod column, yielding 25 g. (50%) of erythro-2-butanol, b.p. 99.2–99.6°, n^{26}D 1.3941.

threo-2-Butanol-3-d_1.—The same procedure starting with cis-2-butene gave in similar yield the threo isomer, b.p. 99.3–99.7°, n^{24}D 1.3950. The infrared spectra of the two deuterated alcohols and of 2-butanol were all distinguishable. The utilization of deuterium could be improved by using a large excess of epoxide, but the work-up was more difficult.

2-Butanol-1-d_3.—Sodium acetate-d_3 (Isotope Specialties Co., 99% deuterated) was converted to acetyl chloride-d_3 by reaction at 0° with phosphorus trichloride in ether followed by distillation; b.p. 50–53°. This was added over a period of 1 hour to a solution at −15° of diethylzinc in ether (prepared from the ethyl Grignard reagent and anhydrous zinc chloride[16]). The solution was heated to boiling

(11) R. R. Johnson and E. S. Lewis, Proc. Chem. Soc., 52 (1958); J. A. Llewellyn, R. E. Robertson and J. M. W. Scott, Can. J. Chem., 38, 222 (1960); K. T. Leffek, J. A. Llewellyn and R. E. Robertson, Abstr. of Papers, 137th Meeting. American Chemical Society, 1960, p. 50-O.

(12) E. S. Lewis, J. L. Kinsey and R. R. Johnson, J. Am. Chem. Soc., 78, 4294 (1956); E. S. Lewis, R. R. Johnson and G. M. Coppinger, ibid., 81, 3140 (1959).

(13) V. J. Shiner, Jr., ibid., 75, 2925 (1953); E. S. Lewis and C. E. Boozer, ibid., 74, 6307 (1952); 76, 791 (1954).

(14) V. J. Shiner, Jr., in V. J. Shiner and E. Campaigne, "Conference on Hyperconjugation," Pergamon Press, New York, N. Y., 1959, p. 159.

(15) H. J. Lucas and D. Pressman, "Principles and Practice in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949.

(16) D. A. Shirley, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, Chap. 2.

for 3 hours, then excess 2 N hydrochloric acid was added and the ether ·layer was separated. Distillation yielded methyl d_3-ethyl ketone in about 26% yield, which was readily reduced to the alcohol with lithium aluminum hydride.

d-Butanol-2.—*sec*-Butyl alcohol was resolved as described previously.[17] The sample used had $[\alpha]^{25}\text{D}$ +12.20°; it was therefore about 89% optically pure.

All chloroformates were made by the methods previously described; 2-butyl chloroformate had b.p. 39–40° (21 mm.). *sec*-Butyl chloride for gas chromatographic reference was made using the Lucas reagent on 2-butanol.

Rate measurements were made as previously described under conditions practically identical with those used for the undeuterated compound, done at the same time and described in reference 2. Thus most systematic errors disappear in considerations of isotope effects.

Substitution Stereochemistry.—Optically active 2-butanol, diluted with racemic 2-butanol, was converted to the chloroformate. In two experiments this was used directly in the gas phase flow apparatus; in two others it was diluted with racemic 2-butyl chloroformate. A very slow flow rate was used to obtain extensive decomposition. The effluent gas stream was passed through a trap containing methanol cooled in Dry Ice. After about 38 hours, the contents of the trap were distilled, first under vacuum at room temperature to remove butenes and hydrogen chloride, then at atmospheric pressure, yielding a fraction boiling 65–68°. The rotation of this fraction was measured and its purity estimated by vapor chromatography. In one case a 4% contamination of 2-butanol was found; in two others, a further dilution with racemic 2-chlorobutane was carried out. Results are expressed below by multiplying the observed rotation (varying from 8 to 0.2°) by factors given parenthetically for the various dilutions as follows: (a) dilution of the starting alcohol (3.66), (b) dilution of the chloroformate (5.52), (c) contamination of the product with impurities (assumed optically inactive) (1.04), (d) dilution of the 2-chlorobutane (6.87). In the following four experiments, the calculated rotations based on optically pure starting

(17) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 1744 (1953).

material are followed by some letters indicating which of the preceding corrections were applied. Experiment 1, corrn. a and c, $[\alpha]^{25}\text{D}$ +34.7°; exp. 2, corrn. a, $[\alpha]^{25}\text{D}$ +34.8°; expt. 3, corrn. a and b, $[\alpha]^{25}\text{D}$ +34.7°; expt. 4, corrn. a, b and d, $[\alpha]^{25}\text{D}$ +35.9°. Reference 9 gives for optically pure 2-chlorobutane $[\alpha]^{25}\text{D}$ 33.8°.

Elimination Stereochemistry.—The same apparatus was used to collect the elimination products in methanol at −80° as was used for the rate measurements and the optical result. The contents of the trap then were allowed to warm to room temperature and the gas phase was sampled in a 20-ml. syringe, which was then used to charge these products to the gas chromatography. The separated olefins were trapped in liquid nitrogen as they came off, and then analyzed for deuterium by mass spectra, kindly performed by Dr. R. Hunt of the Shell Oil Co., Deer Park, Tex. The recording on the gas chromatograph allowed the estimation of the contamination by neighboring olefins. The only contamination found was that of *cis*-olefin by *trans* and *vice versa*. The products from the *erythro* compound were separated on a 4-meter column at 0° with benzyl cyanide saturated with silver nitrate as the stationary phase. The products from the *threo* compound were separated on a 6-meter dioctyl sebacate column at 12° following a 2-meter dioctyl phthalate column at room temperature. Table III

TABLE III

DEUTERIUM CONTENT OF SEPARATED OLEFINS

Stereoisomer	Butene	Atoms D/molecule	Impurities %
erythro	1	1.01	0
erythro	*trans*	0.907	10
erythro	*cis*	0.29	22
threo	1	1.05	0
threo	*trans*	0.00	0
threo	*cis*	0.90	10

shows the results of these experiments, from which Table I was derived. The precision of the last column is not high, it varies both because of the nature of the column and because the point of changing receivers was arbitrary.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM M. RICE UNIVERSITY, HOUSTON, TEX.]

# The Decomposition of Gaseous Chloroformates. III. Rearrangements in the Elimination Reaction[1]

BY EDWARD S. LEWIS AND WILLIAM C. HERNDON

In the gas phase, the thermal decomposition of neopentyl chloroformate yields neopentyl chloride and methylbutenes, but no *t*-amyl chloride. From 1-butyl chloroformate, in addition to 1-chlorobutane and 1-butene, the 2-butenes are also produced. Evidence, based on retention of 1-deuterium, is presented to exclude the intermediacy of divalent carbon compounds. A polar mechanism for elimination is supported.

Introduction

The previous papers in this series[2,3] have been concerned with the kinetics and stereochemistry of the thermal, gas phase decomposition of alkyl chloroformates by the parallel courses 1 and 2.

$$HC-COCCl \longrightarrow \begin{cases} \longrightarrow HC-CCl + CO_2 & (1) \\ \\ \longrightarrow C=C + HCl + CO_2 & (2) \end{cases}$$
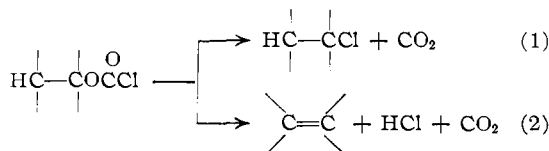
(1) From the Ph.D. thesis of W. C. Herndon, 1958; presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., 1958.

(2) E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

(3) E. S. Lewis, W. C. Herndon and D. C. Duffey, *ibid.*, **83**, 1959 (1961).

A transition state with significant charge separation, especially in the elimination reaction 2, was indicated from substituent and isotope effects, and the latter even suggested an intermediate. A dipolar transition state also has been suggested for the non-chain pyrolytic eliminations from alkyl bromides,[4] and intermediate ion-pairs have been proposed.[5]

In solution, extensive charge separation may be detected since certain carbonium ions rearrange when free or nearly so. Thus, carbonium ion intermediates may be accepted if rearrangement results in these special cases, and can be rejected if only unrearranged products are found. This criterion for the intermediacy of carbonium ions

(4) A. Macoll and P. J. Thomas, *Nature*, **176**, 392 (1955).

(5) C. K. Ingold, *Proc. Chem. Soc.*, 279 (1957).