Evaporative distillation of this material at 65–85° (0.02 mm.) gave 0.703 g. of oil, whose neut. equiv. indicated about 80% of monoester. This fraction gave the same monoanilide, m.p. 117–118°, obtained above.

***trans*-3-Carboxycyclohexaneacetic Acid (IVb).**—From 0.720 g. of IIb, 0.509 g. of crude dimethyl ester IIIb was obtained following procedure (a) above. Evaporative distillation at 70° (0.02 mm.) gave 0.427 g. (52%) of colorless oil, n^{25}_D 1.4593. The saponification of this material (0.383 g.) patterned after the procedure used with the *cis* isomer gave 0.235 g. of crystalline material of wide melting range from which 0.062 g. of pure IVb, m.p. 132.8–134.1°, was obtained as colorless plates after six recrystallizations from water. *Anal.* Calcd. for $C_9H_{14}O_4$: C, 58.1; H, 7.6. Found: C, 58.1; H, 7.6.

Mixtures of IVa and IVb of various compositions melted as follows.

% *cis* (IVa)	M.p., °C.
14.4	121–130
32.5	116–122
45.0	116–131
60.0	118–137
81.3	144–150

Acknowledgment.—A gift from Research Corporation in support of this work is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

The Thermal Decomposition of Ethyl Chlorocarbonate[1,2]

BY LATHROP E. ROBERTS, ROBERT LASHBROOK, MARY J. TREAT AND WILLIAM YATES

RECEIVED JULY 9, 1952

Choppin, Frediani and Kirby[3] found that at temperatures of from 195 to 295° ethyl chlorocarbonate decomposed by a homogeneous unimolecular reaction, with ethyl chloride and carbon dioxide as the only products. We have found that at temperatures of from 280 to 330°, it decomposes by a more complex reaction into ethyl chloride, carbon dioxide, hydrogen chloride and ethylene. Ethylene and hydrogen chloride were formed in approximately equimolecular amounts, and the sum of the percentage of ethyl chloride and either ethylene or hydrogen chloride was approximately equal to that of the carbon dioxide. The reaction was conducted at constant volume and its course followed by recording changes in pressure. Runs made under apparently the same conditions frequently showed different pressure–time relations, although all runs proceeded smoothly. The reaction appears to be sensitive to surface conditions, and when a new reaction flask was used, concordant results could not be obtained until it was thoroughly seasoned. In a total of sixty runs, at temperatures of from 280 to 330°, the ratio of final to initial pressure varied from 2.27 to 2.59, with a mean value of 2.40 and an average deviation from the mean of 0.07. No systematic variation of this ratio with temperature was evident.

While the lack of agreement between runs made under the same conditions has made it impossible to determine mathematically the exact course of the reaction, certain conclusions may nevertheless be drawn. Ethyl chlorocarbonate, in the temperature range studied, does not decompose simply into ethyl chloride and carbon dioxide. The value of the ratio of final to initial pressure would, in itself, rule out such an interpretation. Nor does the ester decompose first into ethyl chloride and carbon dioxide, followed by partial decomposition of ethyl chloride into ethylene and hydrogen chloride. The complete stability of ethyl chloride under the conditions of these experiments, both alone and in the presence of the decomposition products, was shown independently, and is confirmed by the work of Nef.[4] Decomposition may occur by the two simultaneous reactions

(a) $ClCOOC_2H_5 = C_2H_5Cl + CO_2$

(b) $ClCOOC_2H_5 = C_2H_4 + HCl + CO_2$

Such reactions would account for the values of the ratio P_f/P_i found, for the occurrence of ethylene and hydrogen chloride in approximately equimolecular quantities, and for the fact that the percentage of carbon dioxide is approximately equal to the sum of the percentage of ethyl chloride and either ethylene or hydrogen chloride.

However, the bimolecular reaction

$$2ClCOOC_2H_5 = 2CO_2 + HCl + C_2H_5Cl + C_2H_4$$

may also occur. It cannot be the only reaction, since it would demand a ratio P_f/P_i equal to 2.5.

Experimental

Ethyl chlorocarbonate from the Eastman Kodak Company was redistilled twice and the fraction boiling from 90.1 to 90.2° (700 mm.) was used. The reaction was carried out at constant volume in a Pyrex bulb of known volume, and pressures were read on a mercury manometer. The bulb was heated in a manually controlled electric furnace, with temperature control accurate to 0.1°. Prior to each run the heated bulb was exhausted for two hours with a mercury diffusion pump. Weighed amounts of ester were introduced for each run in sealed ampoules, which were broken with a solenoid hammer. Products were removed for analysis with a toepler pump.

Qualitative tests on the products showed the presence of carbon dioxide, hydrogen chloride and unsaturated hydrocarbon, and an inert residue which condensed as a colorless liquid at −72°. After removal of the carbon dioxide and hydrogen chloride, the residual gas absorbed bromine, forming a colorless liquid which melted at 9.3°, and had an index of refraction to sodium light of 1.5363 at 21°. It was evidently slightly impure ethylene bromide. After removal of the ethylene with fuming sulfuric acid, four micro-combustions on the residual gas showed a mean value of 2.0 gram-atoms of carbon for each mole of gas burned, and three determinations of chlorine showed a mean of 1.0 gram-atoms of chlorine per mole. Two determinations of molecular weight by direct weighing gave 67.2 and 66.4. It was concluded that the residual gas was ethyl chloride.

Experiments with mixtures of ethyl chloride, hydrogen chloride, ethylene and carbon dioxide showed that when ethyl chloride was condensed from the mixture, the other gases dissolved in it, hydrogen chloride being almost quantitatively removed from the gas phase. Hence, ethyl chloride could not be determined from the chlorine in the condensate.

The gas mixture was analyzed quantitatively as follows. Hydrogen chloride was absorbed in dilute sodium hydroxide

---

(1) From theses submitted by Robert Lashbrook, Mary J. Curry and William Yates in partial fulfillment of the requirements for the M.S. degree at the University of Arizona.

(2) Presented before the Physical and Inorganic Division of the American Chemical Society, 117th Meeting, April 16–20, 1950, Detroit, Michigan.

(3) A. R. Choppin, H. A. Frediani and G. F. Kirby, THIS JOURNAL, 61, 3176 (1939).

(4) U. Nef, *Ann.*, 318, 14 (1901).

solution, and chloride ion determined volumetrically. It was definitely shown that the presence of ethyl chloride did not affect this determination. Carbon dioxide and hydrogen chloride were then determined together by absorption on ascarite, and carbon dioxide found by difference. The residual gas was analyzed for ethylene by the micro-method of Blacet, MacDonald and Leighton.[5] Ethyl chloride was determined on samples from which carbon dioxide and hydrogen chloride had been removed by exploding the sample with three times its volume of oxygen at reduced pressure, absorbing the liberated chloride ion in sodium hydroxide solution, and titrating. The accuracy of this method was tested on synthetic gas mixtures of composition approximating that of the mixtures resulting from the pyrolyses. The results of a series of representative analyses are shown in Table I. Compositions were found to vary somewhat, as shown, and the variation showed no regular trend with temperature. It may be attributed to the complexity of the reaction, obscure surface effects, and difficulties of analysis.

TABLE I

COMPOSITION OF GAS MIXTURES OBTAINED FROM THE THERMAL DECOMPOSITION OF ETHYL CHLOROCARBONATE

t, °C.	HCl, %	C_2H_4, %	CO_2, %	C_2H_5Cl, %	P_f/P_i
300	16.1	15.0	42.9	27.1	2.31
310	16.1	16.3	41.9	26.0	2.33
320	15.6	17.8	42.0	24.4	2.38
325	16.0	16.4	42.4	24.1	2.31
325	19.9	20.1	41.6	21.5	2.42
330	17.1	18.7	40.8	21.8	2.37
330	20.4	20.9	39.2	18.5	2.46

---

(5) F. E. Blacet, Geo. D. MacDonald and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

Interpretation of the Refractive Index Measurements on the Ternary System RbCl-RbBr-KBr-KCl

BY JOHN E. RICCI

RECEIVED JUNE 4, 1952

The X-ray diffraction study by Wood and Breithaupt[1] of the ternary crystalline solids obtained from mixtures of the salts RbCl, RbBr, KBr and KCl indicated that the salts formed a continuous ternary solid solution as sole solid phase, as was to be expected from the fact that each of the four common-ion binary combinations forms a continuous solid solution with a very shallow minimum in its melting point curve. In consideration of the subtle uncertainty that the X-ray data might not unequivocally distinguish between a single ternary solid solution and a heterogeneous mixture of two common-ion binary solid solutions, the same investigators, in a subsequent study,[2] sought to decide the question by means of refractive index measurements; their article also reports melting point observations on the ternary system further corroborating the conclusion of continuous ternary solid solution. It is claimed that the refractive index data, unlike the X-ray diffraction data, are unequivocal in establishing the nature of the solid as a single homogeneous ternary solid solution. Although the conclusion regarding a continuous ternary solid solution seems to be correct, the argument used is inconsistent and faulty and other accompanying conclusions are incorrect.

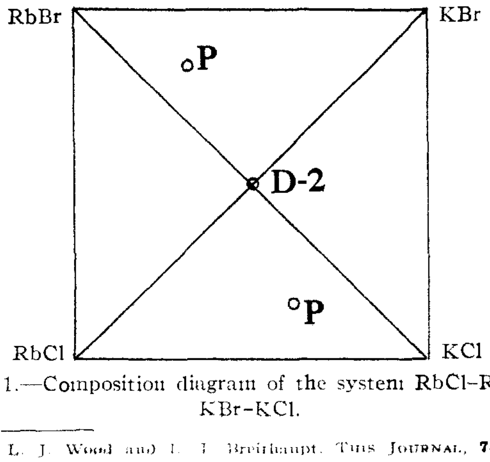

Fig. 1.—Composition diagram of the system RbCl-RbBr-KBr-KCl.

The argument begins with assuming, from a plot of the binary data, that the refractive index of each of the four binary solid solutions, RbCl-RbBr, RbBr-KBr, KBr-KCl and KCl-RbCl (the edges of the composition diagram shown here in Fig. 1), is strictly additive with respect to the refractive indexes of the component salts, and that the resulting ternary solid solution should likewise be additive with respect to two adjacent binary solid solutions. It is expected, in other words, that the refractive index of the ternary solid solution with composition **P** (Fig. 1) should be additive with respect to either the pair of binary solid solutions RbCl-RbBr and RbBr-KBr (possibility A) or the pair RbBr-KBr and KBr-KCl (possibility B). It is furthermore expected that if possibility A holds for point **P**, then point **P′**, for example, will be additive with respect to the pair RbCl-KCl and KCl-KBr and not with respect to the pair RbCl-RbBr and RbCl-KCl. On examining their data on the basis of this expected additivity, the authors conclude that the system is divided according to possibility A, or that all original mixtures in the square of Fig. 1 react to form RbCl and KBr as a "stable salt pair," plus excess of either RbBr or KCl, and that the agreement with the additivity expected on this basis is indeed "striking." Such strict additivity is of course at least as consistent with a heterogeneous mechanical mixture of two binary solid solutions as with any sort of single solid phase formed from them, but heterogeneity is ruled out on the basis of detailed observations reported on "every particle" of the sample D-2 (Fig. 1). Hence the following two conclusions are drawn: (1) that the system forms a single continuous ternary solid solution, and (2) that the refractive index of this continuous solid phase is additive with respect to the salts RbCl-RbBr-KBr on the RbBr side of the diagonal RbCl-KBr and additive with respect to the salts RbCl-KCl-KBr on the KCl side.

These two conclusions, however, are self-contradictory, and the second one is in itself impossible. If the refractive index is represented as a vertical axis upon the composition square of Fig. 1, with **a**, **b**, **c** and **d** as the values of the refractive indexes for the salts RbCl, RbBr, KBr and KCl, respectively.

---

(1) L. J. Wood and L. J. Breithaupt, THIS JOURNAL, **74**, 727 (1952).

(2) L. J. Wood and L. J. Breithaupt, *ibid.*, **74**, 2355 (1952).