

neck flask fitted with a dropping funnel, reflux condenser, and thermometer, was added a mixture of 134.9 g. (0.502 mole) of tetramethyllead and 253.7 g. (0.973 mole) of diethylmercury, while cooling the flask in ice water. An atmosphere of nitrogen was maintained within the system during the addition and for the duration of the experiment. The mixture was kept at 78–83° for four hours, after which it was cooled and allowed to stand at room temperature overnight. The catalyst was extracted by shaking with water; the oily layer was separated and shaken twice with concentrated ammonia solution and finally with distilled water. After filtration through paper to remove traces of water, the product was fractionated³ through a column packed with glass helices. The metal alkyls distilled readily and without decomposition. The various fractions were analyzed for lead and mercury. Figure 1 shows the distillation curve, Table I the analyses, and Table III the composition of the product.

Tetraethyllead and Dimethylmercury.—The above experiment was repeated, starting with 2.0 g. (0.015 mole)

aluminum chloride, 233 g. (1.006 mole) dimethylmercury (which contained 0.001 mole tetramethyllead), and 162 g. (0.498 mole) tetraethyllead. The reaction time was five hours at 80°, and the product stood at room temperature over two nights. Subsequent handling was the same as above. The distillation curve, analyses, and composition of the product are given in Fig. 1 and Tables II and III, respectively.

Summary

Mixtures of diethylmercury with tetramethyllead, and of dimethylmercury with tetraethyllead, containing equal proportions of methyl and ethyl radicals and equivalent amounts of mercury and lead, undergo redistribution and yield the same random equilibrium mixture, in which the mercury shows a greater relative affinity than lead for methyl with respect to ethyl radicals.

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RECEIVED OCTOBER 13, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Redistribution Reaction. IX. Redistribution of Halides and of Esters¹

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As stated in the first paper of this series,² the redistribution reaction is not confined to organometallic compounds, but also has been found to take place in two distinctly different fields, namely, aliphatic halides and esters. So far, the work in these and other fields has been merely exploratory, designed to furnish only a roughly quantitative measure of the occurrence or non-occurrence of redistribution. No attempt has been made to study the influence of the different reaction variables, such as the temperature and amount of catalyst, and no accurate material balances or measurements of the amount of side reaction with the catalyst have been obtained. Further experiments are in progress but, pending future publication of their results, the present paper completes the presentation of the experimental data previously cited.²

In the halides, redistribution was found to occur between ethylene dichloride and dibromide, between ethyl chloride and ethylene dibromide, and between ethyl bromide and ethylene dichloride, in each case using 1.5–3 mole per cent. aluminum chloride as the catalyst.

As shown in Fig. 1 and Table I, in the first of

(1) For paper VIII, see Calingaert, Soroos and Thomson, *THIS JOURNAL*, **62**, 1542 (1940).

(2) Calingaert and Beatty, *ibid.*, **61**, 2748 (1939).

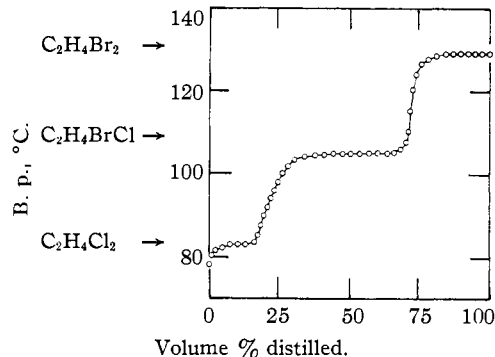


Fig. 1.—Distillation of the reaction product from C₂H₄Br₂ + C₂H₄Cl₂.

these reactions, between the two ethylene dihalides, the composition of the product corresponded within experimental error to a random distribution of the halogen atoms. In this one case, we found later that our result has been fully antici-

TABLE I
PRODUCTS FROM THE REDISTRIBUTION OF ETHYLENE
DICHLORIDE WITH ETHYLENE DIBROMIDE

	Composition, mole per cent.	
	Found	Calcd. ^a for $r^a = 0.467$
C ₂ H ₄ Cl ₂	23.0	21.8
C ₂ H ₄ ClBr	47.4	49.8
C ₂ H ₄ Br ₂	29.6	28.4

^a r is the atomic fraction of chloride found in the product.

pated by Dougherty,³ who stated that the reaction was reversible and that its product corresponded to "the laws of chance." The significance and generality of this statement apparently was not appreciated by either this author or his readers, since no subsequent reports on the subject appear in the literature.

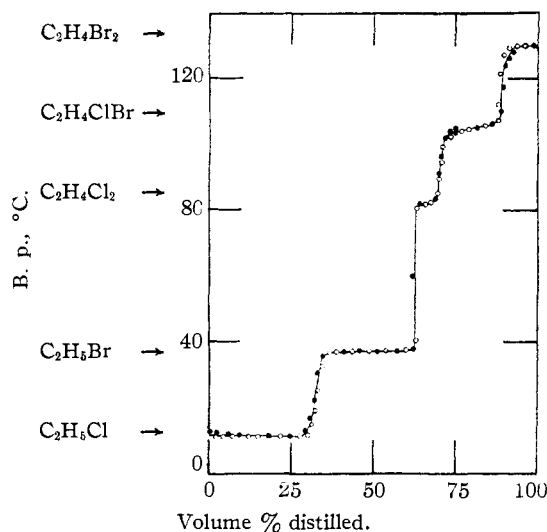


Fig. 2.—Distillation of the reaction product from ●, $C_2H_4Cl_2 + C_2H_5Br$; ○, $C_2H_4Br_2 + C_2H_5Cl$.

In the other two of these reactions, the products, which contained each of the expected five ethyl and ethylene halides, were identical, showing that equilibrium was attained from both sides. The analytical data are shown in Fig. 2 and Table II.

TABLE II

PRODUCTS FROM THE REDISTRIBUTION OF (1) ETHYL CHLORIDE WITH ETHYLENE DIBROMIDE AND (2) ETHYL BROMIDE WITH ETHYLENE DICHLORIDE

	Composition found, mole per cent.	
	(1)	(2)
C_2H_5Cl	35	34
C_2H_5Br	30	29
$C_2H_4Cl_2$	7	9
C_2H_4ClBr	17	18
$C_2H_4Br_2$	11	10

In this case, the composition of the product is not fixed solely by the laws of probability, since it depends on the relative affinities of the two halogens for the ethyl and ethylene radicals, as was shown in paper VIII of this series¹ for the distribution of methyl and ethyl radicals between mercury and lead. Inspection of the data in Table II shows that the relative affinity factor departs slightly from unity, in the direction of a preponderance of ethyl chloride and of ethylene di-

(3) Dougherty, *THIS JOURNAL*, **51**, 576 (1929).

bromide and chlorobromide. At the same time, the three ethylene dihalides as a group within themselves are, as before, present in proportions corresponding to a random equilibrium mixture.

In the ester field, redistribution of the alkoxy radicals was found between dimethyl and dibutyl oxalates, between methyl acetate and ethyl butyrate, and between furfuryl acetate and ethyl furoate, in each case using 3–5 mole per cent. aluminum ethylate as the catalyst and a heating time of five hours at about 100°. Blank experiments showed that, in the absence of the catalyst, no redistribution took place.

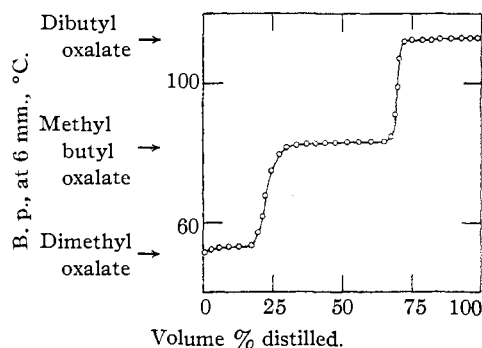


Fig. 3.—Distillation of the reaction product from dimethyl oxalate + dibutyl oxalate.

The first of these three systems, as seen from Fig. 3 and Table III, gave the expected three compounds in just the proportions of a random equilibrium mixture. Here, the accuracy of the analysis was facilitated by the relatively wide spread in the boiling points of the components.

TABLE III

PRODUCTS FROM THE REDISTRIBUTION OF DIMETHYL WITH DIBUTYL OXALATE

	Composition, mole per cent.	
	Found	Calcd. for $r^a = 0.52$
$(COOMe)_2$	28	27
$MeOOCOOCBu$	48	50
$(COOBu)_2$	24	23

^a r is the fraction of methoxyl radicals found in the product.

For the second of these ester systems, the composition of the product again is determined by relative affinities, in this case of the two alkoxy radicals for the two acyl radicals. Inspection of the results, given in Fig. 4 and Table IV, indicates that equilibrium was reached, and that the relative affinity factor in this case is close to unity, giving a symmetrical distribution of the radicals.

The third ester system—furfuryl acetate and ethyl furoate—gave quite similar results (Fig. 5

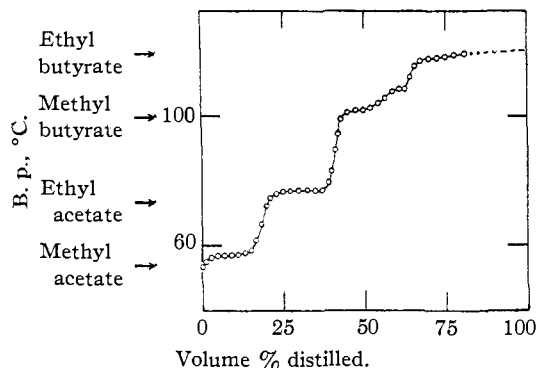


Fig. 4.—Distillation of the reaction product from ethyl acetate + methyl butyrate.

TABLE IV

PRODUCTS FROM THE REDISTRIBUTION OF ETHYL ACETATE WITH METHYL BUTYRATE

	Composition, mole per cent.	
	Found	Calcd. ¹ for $K = 1$, [CH ₃ CO] = 0.50 and [OMe] = 0.45 ^a
CH ₃ COOMe	25.4	22.5
CH ₃ COOEt	23.4	27.5
C ₃ H ₇ COOMe	22.7	22.5
C ₃ H ₇ COOEt	28.5	27.5

^a Concentrations are those taken in the reactants; the [OEt] was augmented by the Al(OEt)₃ used as catalyst.

and Table V), but the data suggest that either equilibrium was not completely attained or else there is a relative affinity factor greater than unity, in favor of the two original compounds.

TABLE V

PRODUCTS FROM THE REDISTRIBUTION OF FURFURYL ACETATE AND ETHYL FUROATE

	Composition found, mole per cent.
Ethyl acetate	23
Furfuryl acetate	24
Ethyl furoate	33
Furfuryl furoate	20

Altogether, it is evident that accurate determinations of equilibria such as these can furnish definite and specific information regarding some of the relative bond strengths in the compounds involved.

Experimental Part

Redistribution of Halides.—A mixture of 49.5 g. (0.5 mole) of ethylene dichloride, 98 g. (0.52 mole) of ethylene dibromide, and 2 g. (0.015 mole) of aluminum chloride was heated to refluxing for two hours. There was some decomposition and liberation of halogen acid. The reaction mixture, after cooling and extracting the catalyst with water, was analyzed by fractional distillation,⁴ using a glass spiral packing in the column.

(4) Calingaert, Beatty and Neal, *THIS JOURNAL*, **61**, 2755 (1939).

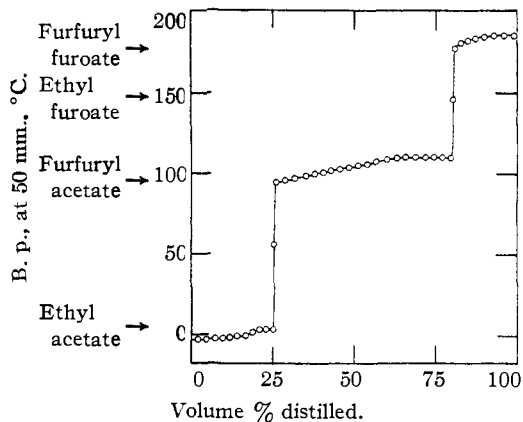


Fig. 5.—Distillation of the reaction product from furfuryl acetate and ethyl furoate.

The redistribution of a 2:1 mixture of ethyl chloride and ethylene dibromide, and of the corresponding mixture of ethyl bromide and ethylene dichloride, was carried out in steel bombs using about three mole per cent. aluminum chloride as catalyst. The mixtures were heated, respectively, to 25° for fourteen days and to 115° for twenty hours. After decomposing the catalyst with water, the products were distilled from the bomb and fractionated.

Redistribution of Esters.—A mixture of 47.2 g. (0.4 mole) of dimethyl oxalate, 80.8 g. (0.4 mole) of di-*n*-butyl oxalate and 5 g. (0.03 mole) of aluminum ethylate⁵ was heated in a small flask to refluxing for five hours. The aluminum ethylate dissolved partially and later a voluminous flocculent white precipitate formed. After cooling in ice water, the reaction mixture was shaken twice with dilute hydrochloric acid. The ester layer was separated, washed with dilute sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The aqueous layer and washings were extracted with several portions of ether, the extracts being combined and dried over sodium sulfate. The main product and ether extracts were subsequently fractionated.

The other ester systems were redistributed in essentially the same manner. The product from the redistribution of methyl butyrate with ethyl acetate was distilled directly from the catalyst, the distillate being subsequently fractionated.

Summary

Experimental data are presented for the redistribution reaction in the following six halide or ester systems: ethylene dibromide and ethylene dichloride, ethyl chloride and ethylene dibromide, ethyl bromide and ethylene dichloride, dimethyl oxalate and dibutyl oxalate, ethyl acetate and methyl butyrate, furfuryl acetate and ethyl furoate.

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RECEIVED DECEMBER 9, 1939

(5) The aluminum ethylate was prepared according to the method described in "Organic Syntheses," XV, 82.