same conditions 10 γ of II caused 100% mortality. It is possible that Bernimolin's I contained II or even that it was not identical with I prepared from II by the method of Brand and Bausch.[2] Bernimolin's assumption that the presence of I (perhaps formed by irradiation of II) may be partly responsible for the extraordinary residual effect of II cannot be correct. Likewise Bernimolin's conclusion, based on the supposed insecticidal activity of I, that the molecular weight of residually active contact insecticides of the halohydrocarbon type is not limited, is without foundation.

The alteration of physical properties, *e.g.*, the decrease in lipoid solubility, with increase in molecular weight corresponds in our experience[3] with a quite general lowering of contact insecticidal activity of halogenated hydrocarbons when their molecular weight exceeds 430–450. Halogenated hydrocarbons whose molecular weight exceeds this limiting value are not necessarily completely inactive as contact insecticides. Thus in 1947 we reported[4] insecticidal activity for the substance M 490 (so called because of its approximate molecular weight). This activity, however, was much less than that of M 410[5] (Chlordane).

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(2) Brand and Bausch, *J. prakt. Chem.*, **127**, 232 (1930).

(3) R. Riemschneider, "Zur Kenntnis der Kontakt-Insektizide I," Beiheft 2, Ergänzungsband 1 zur "Pharmazie" 1947. A paper of Lord (*Ann. Appl. Biol.*, **35**, 505 (1948)) confirms the supposition made in this book that the molecular weight of highly active contact insecticides of the halohydrocarbon type with residual effect is limited.

(4) Riemschneider, *Mitt. Physiol. Chem. Inst.*, *R***12**, Dec., 1947, and *R***11**, Oct., 1947.

(5) Riemschneider, *Pharmazie*, **3**, 115 (1948); *Chem. Z.*, II, 344 (1948); *Chim. et Ind.*, **64**, 695 (1950).

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The System $Ba(IO_3)_2$–$BaCl_2$–H_2O at 25°

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In connection with studies on the aqueous phase relations of the halates, the 25° isotherm of the system $Ba(IO_3)_2$–$BaCl_2$–H_2O was investigated, revealing the formation of an incongruently soluble hydrated double salt with the probable formula $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$. The results, in terms of weight percentage, are listed in Table I and plotted in Fig. 1.

The general procedure was that described in similar reports. Complexes were made up from water and the solids $Ba(IO_3)_2 \cdot H_2O$ and $BaCl_2 \cdot 2H_2O$, which were C.P. samples checked for purity by direct analysis. After 1 or 2 weeks of stirring the filtered saturated solution was analyzed for iodate with standard thiosulfate and for total solid by evaporation. Reanalysis after a similar additional period of stirring was used to prove equilibrium. The double salt did not form readily. A practically complete but metastable diagram was obtained with the separate hydrated salts as sole solid phases, before the double salt, suspected because of unsatisfactory aspects of the first diagram, could be made to form; thereafter it was used to seed the various complexes. After such seeding, for example, the remaining liquid of complex no. 6 dropped in composition to that shown as line 8 of the table; the "total complex" composition for line 8 was estimated from that of no. 6 corrected for the amount of liquid withdrawn for analysis before seeding. Line 9 bears the same relation to line 7.

TABLE I

SYSTEM $Ba(IO_3)_2$–$BaCl_2$–H_2O AT 25°

	Saturated solution Wt. %			Total complex wt. %		
	$Ba(IO_3)_2$	$BaCl_2$	Density	$Ba(IO_3)_2$	$BaCl_2$	Solid phase^{b}
1	0.0400	0.00	0.997	...	0.00	A
2	.0189	19.63	1.194	8.00	18.00	A
3	.0187	20.50	1.206	25.99	14.99	A
4	.0198	21.56	1.218	7.00	20.00	A
5	.0231	25.29	1.268	23.82	19.07	A^{m}
6	.0240	25.59	1.273	23.52	21.47	A$^{m\ a}$
7	.0267	27.09	1.286	23.58	21.54	(A + C)^{m}
8		22.06	1.222	35.3	19.6	A + B
9		22.05	1.223	29.5	20.2	A + B
10	.0201	(22.38)?		6.01	21.36	A + B
11	.0201	22.06	1.225	6.03	22.16	A + B
	.0201	22.06	1.223	= average		A + B
12	.0189	22.72	1.232	6.03	23.24	B
13	.0186	23.76	1.245	5.99	24.17	B
14	(.020)	24.25	1.255	10.96	24.96	B
15	.0179	24.73	1.258	6.00	25.04	B
16	.0171	25.45	1.266	6.00	25.72	B
17	(.019)	25.51	1.269	10.02	25.96	B
18	.0165	26.01	1.274	6.04	26.22	B
19	.0152	26.82	1.285	5.89	26.95	B
20	.0153	27.09	1.289	4.99	27.95	B + C
21	.0153	27.11	1.289	2.00	39.95	B + C
22	.00	27.11	1.289	0.00	...	C

[a] Probably in course of change, not completely at equilibrium. [b] A = $Ba(IO_3)_2 \cdot H_2O$; B = $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$; C = $BaCl_2 \cdot 2H_2O$; *m* = metastable.

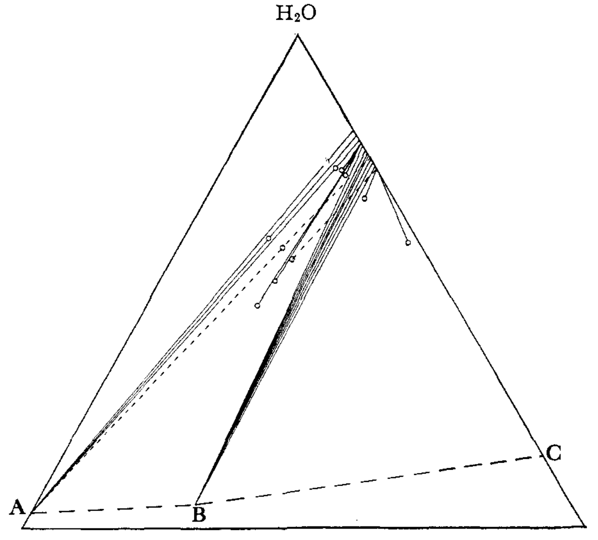

Fig. 1.—25° isotherm of system $(BaIO_3)_2$–$BaCl_2$–H_2O; A = $Ba(IO_3)_2 \cdot H_2O$, B = $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$, C = $BaCl_2 \cdot 2H_2O$.

The formula of the double salt was determined by the intersection of the tie-lines fixed by the compositions of saturated solution and total complex.[1] For greater dependability of the extra-

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(1) A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

polation the two runs numbered 14 and 17 were made with much larger amounts of solid to be transformed into double salt, and these were rotated for about a year before analysis. Although the equimolar ratio of the salts in the compound is quite clear from mere graphical extrapolation, it is more difficult to fix the hydration of the double salt, since the weight percentages of water in the mono-, di- and trihydrates of a 1:1 double salt are not very different, being 2.53, 4.93 and 7.21, respectively.

The tie-lines for complexes 12–19, in which the double salt was the sole saturating solid, were extrapolated algebraically to their intersections with the line representing the 1:1 salt ratio. The average number of moles of H_2O per $Ba(IO_3)_2 \cdot BaCl_2$ thus calculated is 2.13 with an average deviation from the mean of 0.18. The tie-lines were also extrapolated to the line representing the percentage of $Ba(IO_3)_2$ in a 1:1 double salt with 1, 2 and 3 moles of H_2O, respectively, in the formula. The intersections of the tie-lines with each of these fixed lines was then expressed as an "error" in terms (positive or negative) of percentage of $BaCl_2$ in the solid. The average (algebraic) error of extrapolation is then -0.71% $BaCl_2$ at the monohydrate, -0.08% at the dihydrate and $+0.52\%$ at the trihydrate.

The various tie-line extrapolations therefore seem to be sufficient to justify accepting the formula $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ for the double salt. The other solid phases of the isotherm are $Ba(IO_3)_2 \cdot H_2O$ and $BaCl_2 \cdot 2H_2O$.

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Exchange of Deuterium Oxide with Bromodichloromethane and Chlorodibromomethane

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The base-catalyzed exchange of trichloromethane with deuterium oxide has been studied by Sakamoto,[1] who found that the rate of exchange was rapid compared with the rate of hydrolysis. Hine,[2] in a study of the basic hydrolysis of trichloromethane, proposed mechanisms involving the intermediates CCl_3^- and CCl_2 which were in concordance with the observed rapid exchange rates reported by Sakamoto. Newton and Rollefson[3] utilized the base-catalyzed exchange reaction as a method of preparation of trichloromethane-*d*.

Bromodichloromethane-*d* and chlorodibromomethane-*d* have been obtained in this Laboratory by the exchange reaction between the protium analogs and deuterium oxide in the presence of deuteroxide ion.[4] The reactions were carried out in heavy-walled Pyrex vessels of about 30 ml. volume, into which were placed 0.1 mole of purified halomethane, 0.1 mole of 98% deuterium oxide and 0.01 mole of sodium deuteroxide. After outgassing the contents at −78°, the vessel was sealed and maintained at 105° in the absence of light for four days, with periodic shaking. The reactor was then cooled to −195° and opened. The non-aqueous layer was dried and distilled through a small packed column.

The infrared absorption spectra of the purified products revealed appropriate bands attributed to the C–D bond stretching and bending vibrations. A determination of the isotopic purity of the deuterohalomethanes was carried out on the basis of the 3020 cm.$^{-1}$ band of the C–H bond. The results were 43% CBr_2ClD and 16% CCl_2BrD. Upon recharging the reactor with the enriched compound and a new supply of deuterium oxide and sodium deuteroxide in the original proportions the exchange reactions were repeated under similar conditions, resulting in 64% CBr_2ClD and 36% CCl_2BrD, respectively.

Considerable gas pressure (non-condensable at −195°) was observed at the end of each run. In one control experiment of two days using CBr_2ClH, the non-condensable gas was analyzed mass-spectrometrically and found to be essentially pure carbon monoxide, in a quantity accounting for approximately 3.5% of the total halomethane used. The aqueous phase was acid. The total halide ion found in the aqueous phase[5] corresponded to about 3% halomethane decomposition. In several experiments the ratio of Br^- to Cl^- exceeded 2:1. This ratio was found to vary; no explanation has yet suggested itself.

In one experiment of 16 days with CBr_2ClH, the total halide ion recovered was 10.5 millimoles; originally 11.8 millimoles of deuteroxide ion was available. This ratio of OD^-/X^- of 1.12 is in reasonable agreement with the stoichiometry of the hydrolysis according to the mechanisms of Hine.[2] The over-all reaction for decomposed halomethane may be written: $2CX_3H + 7OH^- = CO + 6X^- + HCO^-_2 + 4H_2O$, so that the ratio of hydroxyl consumed to halide produced would be 7/6 or 1.17. It thus appears that the extent of decomposition is limited by the hydroxyl ion available. It should also be noted that both of the purified halomethanes (and their deuterium analogs) were extremely stable to heat and light in the absence of oxygen, in contrast to the decomposition usually observed when exposed to the atmosphere.

It is clear from these results that the rate of exchange of bromodichloromethane and chlorodibromomethane is indeed more rapid than the rate of hydrolysis, in agreement with the previous data for chloroform. However, the apparent order of reactivity toward exchange for these two compounds is somewhat surprising from a point of view of electronegativity. Further kinetic studies in a single phase system appear necessary for an understanding of this observation.

Thanks are due to D. V. Kniebes, S. Katz and V. H. Dibeler for their valuable assistance. The D_2O

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(1) Y. Sakamoto, *Bull. Chem. Soc. Japan*, **11**, 627 (1936).

(2) J. Hine, THIS JOURNAL, **72**, 2438 (1950).

(3) T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

(4) The procedure of ref. 3 employed carbonate as the base and was found to be unsatisfactory in the case of the bromomethanes. The carbonate was completely decomposed, resulting in explosion of the reaction vessels.

(5) The concentrations of Br^- and Cl^- ions in the aqueous phas were obtained by potentiometric titration with silver nitrate.