may partially determine the composition of the hydrolysis products.

Effect of Solvent on the Reaction of Zinc with Butenyl Bromides.[11]—In order to determine whether or not the composition of the butene mixtures prepared by the action of zinc on butenyl bromide mixtures[2a] in 80% ethanol was independent of the character of the solvent, we have allowed zinc to react with a butenyl bromide mixture rich in primary bromide and with one rich in secondary bromide using absolute ethanol and absolute isopropanol as solvents. The four dibromobutane mixtures obtained from the butene mixtures were analyzed by the reaction rate method. The average analysis for the four samples was 60.3% 1-butene, 31.8% *cis*-2-butene and 7.9% *trans*-2-butene compared with 62.1, 30.5 and 7.5% found with the 80% ethanol. Hence we see that the change in solvent has had little or no effect.

[11] We were aided in this work by Mr. Abe Lasher and Mr. Norman Kaufman.

Summary

Optimum conditions are reported for obtaining excellent yields of butenylmagnesium chloride.

Butene mixtures have been prepared from the reaction of different mixtures of butenyl (crotyl and methylvinylcarbinyl) chlorides with (1) magnesium in diethyl ether followed by hydrolysis, and (2) zinc in boiling 80% ethanol. Allylic rearrangements during the reactions led to butene mixtures which are independent of the composition of the butenyl chloride mixtures but dependent on the character of the metal and solvent.

Magnesium gives the same butene mixture from butenyl chloride as from the corresponding bromide.

Zinc gives a butene mixture from butenyl chloride which is similar to but definitely different than the butene mixture from butenyl bromides.

Absolute ethanol and isopropanol give the same results as 80% ethanol when used as a solvent for the reaction of zinc with butenyl bromides.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Inorganic Oxychlorides as Hydrogen Bonding Solvents

BY L. F. AUDRIETH AND R. STEINMAN

The present investigation was undertaken to determine if inorganic acid chlorides containing oxygen atoms of potential donor ability are capable of bonding with compounds containing an acceptor hydrogen to form the C—H←O linkage. In order to evaluate the influence of the highly negative chlorine atoms in the acid chlorides, it also became necessary to compare the observed effects with those of certain related organic compounds whose behavior has not been ascertained heretofore. The experimental study involved specifically the determination of the heats of mixing of phosphorus oxychloride, sulfuryl chloride, thionyl chloride, diethyl carbonate, diethyl sulfite, diethyl sulfate, and propionyl chloride with chloroform and with carbon tetrachloride.

Experimental

The calorimeter and method employed in carrying out the heat of mixing measurements were those described and employed previously by Zellhoefer and Copley.[1]

All compounds were purified by fractional distillation. Constancy of boiling point as well as of refractive index, where possible, were taken as a measure of purity. Care was taken to ensure pure, dry samples by storing them in a dark cupboard in glass-stoppered bottles over chemically inert drying agents. The refractive indices were frequently rechecked and the compounds redistilled when they began to deteriorate.

Propionyl chloride was prepared from benzoyl chloride and propionic acid.[2] Commercial samples were invariably found to contain thionyl chloride which could not be removed successfully by fractional distillation. Thionyl chloride boils at 78.8°, propionyl chloride at 80°.

Discussion of Results

The high heats of mixing of inorganic acid chlorides with chloroform as acceptor solvent give definite evidence of hydrogen bonding. This conclusion is verified by the fact that solution of these same compounds in carbon tetrachloride is accompanied by only a small temperature change—slight heat effect with phosphorus oxytrichloride and a barely observable cooling effect with thionyl chloride and sulfuryl chloride. The

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[1] Zellhoefer and Copley, THIS JOURNAL, **60**, 1343 (1938).

[2] H. C. Brown, *ibid.*, **60**, 1325 (1938).

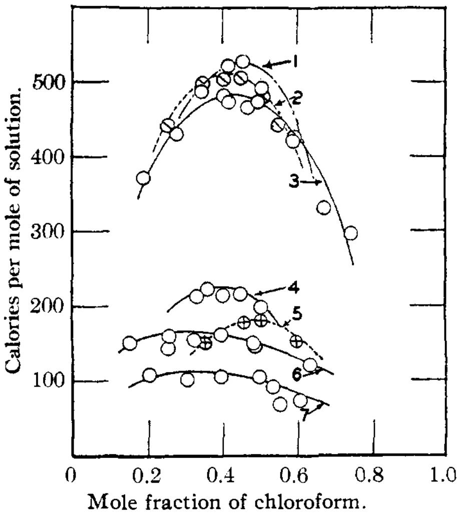

Fig. 1.—Heat of mixing in calories per mole of solution of chloroform with: 1, diethyl carbonate; 2, diethyl sulfite; 3, phosphorus oxychloride; 4, diethyl sulfate; 5, propionyl chloride; 6, sulfuryl chloride; and 7, thionyl chloride.

values for the peaks of the heat of mixing–composition curves (see Fig. 1) at the corresponding mole fractions of solute in chloroform are given in Table I.

TABLE I

HEATS OF MIXING OF INORGANIC OXYCHLORIDES AND THEIR ESTERS WITH CHLOROFORM

	Heat of mixing per mole of solution in g. cal. at 3°	Mole fraction of donor
Phosphorus oxychloride	482	0.429
Triethyl phosphate[3]	1100	.409
Sulfuryl chloride	166	.310
Diethyl sulfate	224	.389
Thionyl chloride	112	.328
Diethyl sulfite	505	.397
Propionyl chloride	180	.504
Diethyl carbonate	523	.446

In order to ascertain the relative effect of chlorine atoms upon the donor ability of the oxygen atoms, the heats of mixing of the corresponding organic esters with chloroform were determined. The results of these measurements (see Fig. 1 and Table I) demonstrate that substitution of ethoxy groups for chlorine atoms gives compounds which exhibit a higher heat of mixing with chloroform, and indicate also that the chlorine atoms definitely decrease the donor ability of the semi-polar oxygen in forming hydrogen bonds. In each case, mixing of the ester with carbon tetrachloride either gave no heat effect, or caused very slight cooling to take place.

Glasstone[4] had already ascribed the difference in hydrogen bonding ability of diethyl ether and of β,β'-dichloroethyl ether, respectively, with chloroform, to the electron attracting nature of the chlorine atoms in decreasing the donor ability of the oxygen. Our results may be regarded as further evidence for the validity of the Glasstone postulate. The effect of chlorine upon the hydrogen bonding ability of potential donor solvents is also evident from a comparison of the heat of mixing curves of chloroform with diethyl carbonate and with propionyl chloride, respectively (Fig. 1). There is a markedly lower heat of mixing with the latter compound in which a chlorine atom is adjacent to the carbonyl group containing the donor oxygen.

Summary

Heat of mixing measurements of inorganic oxychlorides with chloroform indicate that hydrogen bonding takes place involving formation of the C—H←O linkage. The strength of this bond is materially decreased by the presence of chlorine atoms in the donor molecule. The corresponding esters, in which the chlorine atoms are replaced by the less negative ethoxy groups, are very much better hydrogen bonding solvents.

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(3) Marvel, Copley and Ginsberg, THIS JOURNAL, **62**, 3109 (1940).

(4) Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937).