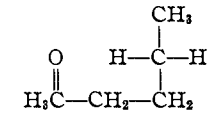
of carbon monoxide to increase from 0.26 at 15° to 0.37 at 100° in the vapor phase whereas the yield in paraffin solution increased from 0.01 to 0.30 in the same temperature interval. The difference between the two cases may be due to the Franck–Rabinowitch effect. The yield of ethylene decreased in both cases with increase in temperature, but the change was not very pronounced. Thus the general phenomena in di-*n*-propyl ketone and in methyl *n*-butyl ketone are similar.

The formation of acetone and propylene in what appears to be a single step with yield independent of temperature is an interesting phenomenon. Possibly methyl *n*-butyl ketone can exist in a cyclic form through hydrogen bonding



which might be expected to dissociate into the enol form of acetone and propylene in a single step. The quantum yield of 0.5 might indicate 50% of the molecules to be in this form but, if this is correct, the independence of temperature is surprising.

By placing deuterium atoms on the γ-carbon only it might be possible to obtain evidence for the cyclic mechanism if the acetone can be shown to possess one deuterium atom per molecule. Deuterium atoms in other positions would not lead to deuteriated acetone if the picture is valid.

It should be possible to put C^{14} in the two α-positions and in the carbonyl group. In this case every molecule of acetone should have three radioactive carbon atoms.

Experiments of these two types are to be undertaken as soon as circumstances permit.

Summary

1. Methyl *n*-butyl ketone gives a quantum yield of acetone production of about 0.5 independent of temperature from 25 to 300°.

2. The quantum yield of carbon monoxide formation increases markedly with temperature.

3. One molecule of propylene is produced for each molecule of acetone at room temperature, but the yields of propylene and of several other hydrocarbons increase markedly with temperature.

4. Acetone is not formed from a recombination reaction or any other reaction involving acetyl radicals since the latter are too unstable at the higher temperatures employed.

5. It is probable that acetone and propylene with quantum yields of about 0.5 are formed in the primary step whereas the remainder of the absorbing molecules either give radicals which eventually produce carbon monoxide or have the energy degraded into vibrational energy. Increase in the thermal energy of the absorbing molecules increases the probability of this type of decomposition.

ROCHESTER, NEW YORK RECEIVED APRIL 25, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE PITTSBURGH PLATE GLASS CO., COLUMBIA CHEMICAL DIVISION]

A Study of the Reaction of Alcohols with Thionyl Chloride[1]

BY WILLIAM E. BISSINGER AND FREDERICK E. KUNG

As illustrated in the following equations, thionyl chloride has been reported[2–7] to undergo a wide variety of reactions with alcohols in the absence of hydrogen chloride acceptors.

$$SOCl_2 + ROH \longrightarrow ROSOCl + HCl \quad (1)$$
$$ROSOCl + ROH \longrightarrow R_2SO_3 + HCl \quad (2)$$
$$SOCl_2 + 2ROH \longrightarrow R_2SO_3 + 2HCl \quad (3)$$
$$R_2SO_3 + SOCl_2 \longrightarrow 2ROSOCl \quad (4)$$
$$ROSOCl \longrightarrow RCl + SO_2 \quad (5)$$
$$SOCl_2 + ROH \longrightarrow \text{olefin} + 2HCl + SO_2 \quad (6)$$

In some of these reactions considerable disagreement exists with regard to the reaction products and the yields obtained.[7,8,9] The most serious discrepancies are found in the results obtained from the reaction of secondary alcohols with thionyl chloride. For example, although Voss and Blancke[10] have reported the preparation of isopropyl chlorosulfinate in 46% yield, Gerrard[8] has claimed a 75–80% yield, while Libermann[7] stated that "only very small quantities" of impure isopropyl, *s*-butyl, and *s*-octyl chlorosulfinates could be obtained from the direct reaction of these alcohols with thionyl chloride. Another controversy over the preparation of cyclohexyl sulfite from cyclohexyl alcohol and thionyl chloride was recently disposed of by Kyrides.[9] Some factors which may be responsible for these anomalies are (a) the frequent failure of various workers to present experimental details, (b) the sensitivity of some of these reactions to small changes in experimental conditions due to (c) the known thermal instability of the alkyl chlorosulfinates and (d) the previously unreported rapid rate of reaction of sulfite esters with hydrogen chloride. In

(1) Presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, April 17, 1947.

(2) Carius, *Ann.*, **111**, 95 (1859).

(3) Stahler and Schirm, *Ber.*, **44**, 319 (1911).

(4) Geuther and Roschlau, *Ann.*, **224**, 223 (1884).

(5) Voss, German Patent 487,253; *C. A.*, **24**, 2149 (1930).

(6) Carré and Libermann, *Bull. soc. chim.*, [4] **53**, 1051 (1933).

(7) Libermann, *Ion.* **4**, 811 (1944).

(8) Gerrard, *J. Chem. Soc.*, 218 (1940).

(9) Kyrides, THIS JOURNAL, **66**, 1006 (1944).

(10) Voss and Blancke, *Ann.*, **485**, 258 (1931).

connection with item (d), we have observed that *n*-propyl and isopropyl sulfites dissolved considerable hydrogen chloride and underwent a rapid reaction with this material at 65–70° as shown in the equation

$$R_2SO_3 + HCl \longrightarrow RCl + ROH + SO_2 \quad (7)$$

The corresponding chlorosulfinates, on the other hand, dissolved very little hydrogen chloride, and their rate of decomposition was not altered by this gas. The instability of sulfite esters to hydrogen chloride therefore makes it desirable to remove this gas as rapidly as formed in the reaction of alcohols with thionyl chloride. Although other workers[3,9–11] have developed methods which would lead to the rapid removal of hydrogen chloride, no one appears to have recognized the existence of reaction 7. The process which we developed for the elimination of hydrogen chloride involved the simultaneous addition of the alcohol and thionyl chloride over the same period of time to a large amount of a refluxing solvent in which the reactants and products (except hydrogen chloride and sulfur dioxide) were soluble. While thereby maintaining the hydrogen chloride concentration constant and at a minimum, we have studied the effect of varying the temperature, ratio of reactants, and structure of alcohols on the yields and types of products obtained. The reaction temperatures ranged from 12 to 180° while the molar ratio of alcohols to thionyl chloride varied from 4:1 to 1:6. The alcohols selected as being representative of simple primary, secondary, and tertiary alcohols were *n*-propyl, isopropyl and *t*-butyl alcohols.

Experimental

Preparation of Materials.—The alcohols, obtained from the following sources, were of high purity and were used without further purification: *n*-propyl alcohol (Eastman Kodak Co. white label), isopropyl alcohol (Carbide and Carbon—99.2% isopropyl alcohol), *t*-butyl alcohol (Eastman yellow label). The thionyl chloride was a purified grade manufactured by this Division and used without further rectification.

For the preliminary studies the first samples of sulfites were prepared by the method of Suter and Gerhart[12] while the chlorosulfinates were obtained by the procedure of Carré and Libermann.[13] These materials, all of which have been previously reported,[3,6,8,14] were fractionated through a 1.7 × 20-cm. Fenske column under the following conditions: *n*-propyl sulfite, b. p. 73–74° (10 mm.); isopropyl sulfite, b. p. 68–69° (20 mm.); *n*-propyl chlorosulfinate, b. p. 37–38° (10 mm.); isopropyl chlorosulfinate, b. p. 39–40° (20 mm.).

Stability of Propyl Sulfites and Chlorosulfinates to Hydrogen Chloride.—Before determining the effect of hydrogen chloride, control tests were run in which freshly distilled, 100-g. samples of the esters were stored in loosely stoppered flasks at various temperatures and then redistilled to determine the amount of decomposition. In conducting the stability tests with hydrogen chloride, 100 g. of the freshly distilled ester was placed in a 125-ml., three-necked flask fitted with a sealed stirrer, thermometer, inlet tube and exit tube, to which was connected a Dry Ice trap. With stirring, anhydrous hydrogen chloride was passed into the liquid throughout the reaction period. The material in the Dry Ice trap and that remaining in the reaction vessel was fractionated as before. The results are shown in Table I. In several preliminary experiments the solubility of hydrogen chloride in *n*-propyl sulfite and chlorosulfinate was approximated by passing the gas through the esters at 3–6°, and 65–70° while observing the weight increases. At 3–6°, the chlorosulfinate, 100 g., dissolved 3 g. of hydrogen chloride from 10 g. introduced, while the sulfite, 83 g., dissolved all of the 25 g. of hydrogen chloride introduced. At 65–70° the chlorosulfinate dissolved no measurable amounts while the sulfite, 100 g., dissolved 25 g. of hydrogen chloride from 33 g. introduced.

TABLE I

EFFECT OF HYDROGEN CHLORIDE ON PROPYL SULFITES AND CHLOROSULFINATES

Compound	Moles	HCl introduced, moles	Temp., °C.	Time, hr.	Decomposed, %
n-PrOSOCl	0.70	None	25–30	192	6
n-PrOSOCl	.70	None	70	15	10
n-PrOSOCl	.70	1.4	65–70	15	11[a]
i-PrOSOCl	.70	None	25–30	144	69
i-PrOSOCl	.70	None	60	3	40
i-PrOSOCl	.70	1.25	60	3	44
n-Pr_2SO_3	.60	None	70	15	2[b]
n-Pr_2SO_3	.60	0.90	65–70	15	40[c]
i-Pr_2SO_3	.60	None	70	15	2[b]
i-Pr_2SO_3	.60	0.80	65–70	12	100[d]

[a] Distillation of the Dry Ice trap material gave 2.4 g. of *n*-propyl chloride, b. p. 45–46° (40% yield, based on extent of decomposition). [b] Probably mechanical loss and not decomposition. [c] Distillation gave 7.4 g. of *n*-propyl chloride, b. p. 44–45°, and 10 g. of *n*-propyl alcohol, b. p. 93–96°, respective yields of 39 and 70%, based on decomposition. [d] Distillation gave 20 g. (43% yield) of isopropyl chloride, b. p. 33–39°, and 21 g. (58% yield) of isopropyl alcohol, b. p. 78–82°.

Reaction of Thionyl Chloride with Alcohols in a Refluxing Solvent.—The apparatus consisted of a 1000-ml., four-necked flask fitted with a reflux condenser, sealed stirrer and two graduated dropping funnels. Five hundred ml. of the solvent was placed in the flask and maintained at reflux throughout the reaction period. The approximate reaction temperatures were determined by the boiling points of the solvents: C_2H_5Cl (12°), CH_2Cl_2 (42°), $CHCl_3$ (61°), CCl_4 (76°), $SOCl_2$ (78°), C_6H_5Cl (132°), and o-$C_6H_4Cl_2$ (179°). The alcohol and thionyl chloride were then added simultaneously at constant rates, with the addition of the two reactants being completed in the same time. The addition period required one to three hours after which the refluxing was continued for three to five hours more. The evolved gases were passed through distilled water, then a cold 25% sodium hydroxide solution, a calcium chloride drying tube, and finally a Dry Ice trap. The products in the reaction flask were generally distilled immediately after the reflux period. Distillation was conducted through the 1.7 × 20-cm. Fenske column, partially reduced pressure being utilized to prevent heating of the mixture above that used during the reaction proper. While this distillation gave the yields of sulfite and chlorosulfinate esters, the more volatile products of the reaction were identified as shown in the next section.

Identification and Determination of Yields of Alkyl Chlorides, Olefins and Diisopropyl Ether.—The yield of *n*-propyl chloride was obtained indirectly, by measuring

(11) Arbuzov, *J. Russ. Phys.-Chem. Soc.*, **41**, 429 (1909); *Chem. Zentr.*, **80**, II, 684 (1909).

(12) Suter and Gerhart, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 112.

(13) Carré and Libermann, *Compt. rend.*, **196**, 1419 (1933).

(14) Strecker and Spitaler, *Ber.*, **59**, 1770 (1926).

the amount of sulfur dioxide evolved during the reaction, as a result of the occurrence of reaction 5. The only other sources of sulfur dioxide (reactions 6, 7) were eliminated because olefin and ether formation did not occur. The determination of **isopropyl chloride** in a similar manner was more complicated since reactions 5, 6, and 7 occurred simultaneously. The yield of isopropyl chloride was obtained by measuring all sulfur dioxide evolved while accurately determining the yields of propylene and diisopropyl ether by distillation; by subtracting the amount of sulfur dioxide formed as a result of olefin and ether formation from the total amount of sulfur dioxide evolved, the yield of isopropyl chloride was arrived at. Qualitative support for this method of analysis resulted from the actual isolation by distillation of *n*-propyl and isopropyl chlorides in a number of experiments.

The *t*-butyl chloride was present as an oil layer distributed among the several aqueous traps. Its yield was determined by isolation and distillation.

The **propylene** was always found in the Dry Ice–acetone trap. Its yield was determined by distillation. The propylene was further identified by bromination, yielding 1,2-dibromopropane, b. p. 136–140°. The **isobutylene**, which was collected in the Dry Ice–acetone trap, was likewise distilled to determine its yield. As further identification, it was converted to isobutylene dibromide, b. p. 64–67° at 47 mm., $n^{20}D$ 1.5082; this was hydrolyzed by refluxing with water for two hours and the isobutyraldehyde converted to its 2,4-dinitrophenylhydrazone, m. p. 180°.

The **diisopropyl ether** was found in the lower boiling fractions, b. p. 33–128°, from the distillation of the crude reaction product. Careful refractionation of the material collected at 63–81° through a 1.1 × 45-cm. Fenske column isolated the diisopropyl ether fraction, b. p. 65–65.5°, $n^{20}D$ 1.3710, d^{20}_4 0.744.[15]

The results are illustrated graphically in Figs. 1–8, the yields reported for the individual products being placed on an additive scale.

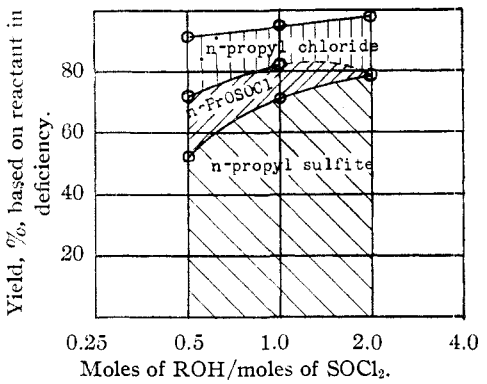


Fig. 1.—Yields of products from *n*-propyl alcohol as a function of ratio of alcohol to thionyl chloride at 40°.

Stability of Isopropyl Sulfite at 130°.—A mixture of 106.7 g. (0.64 mole) of freshly distilled isopropyl sulfite in 300 ml. of chlorobenzene was refluxed at 130° for four hours and then distilled. No diisopropyl ether or other products boiling below chlorobenzene was obtained.

Discussion of Results

Development of the refluxing solvent technique for the rapid removal of hydrogen chloride afforded an **easily reproducible** method for investigating the reaction of various alcohols with thionyl chloride at different temperatures and with varying molar ratios of reactants. As would be expected from the scope of this work, examples of every known type of reaction, as represented by equations 1–6, were encountered. In addition, a previously unreported reaction, ether formation, was observed with isopropyl alcohol under certain conditions.

(15) A sample of refined grade diisopropyl ether (Shell Chemical Co.) had b. p. 66–67°, $n^{20}D$ 1.3698, d^{20}_4 0.725.

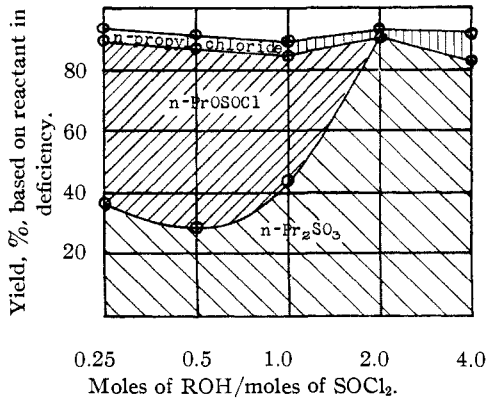


Fig. 2.—Yields of products from *n*-propyl alcohol as a function of ratio of alcohol to thionyl chloride at 180°.

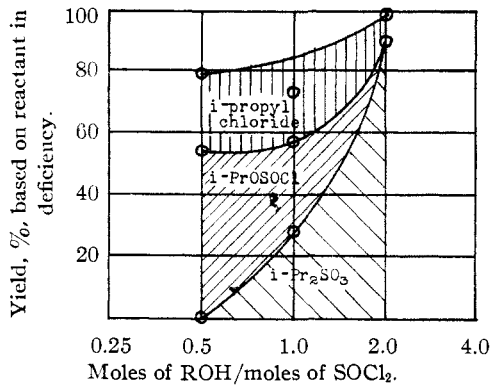


Fig. 3.—Yields of products from isopropyl alcohol as a function of ratio of alcohol to thionyl chloride at 40°.

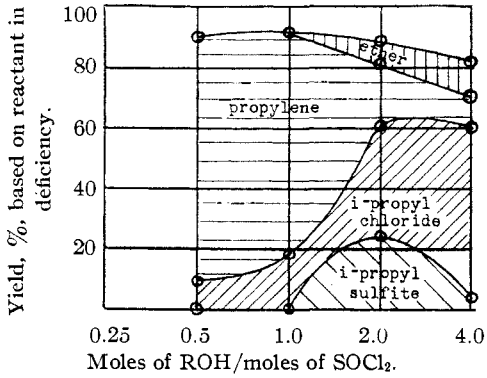


Fig. 4.—Yields of products from isopropyl alcohol as a function of ratio of alcohol to thionyl chloride at 180°.

Effect of Variables

Temperature.—At temperatures of 40 and 76° the predominant products from the reaction of thionyl chloride with primary and secondary

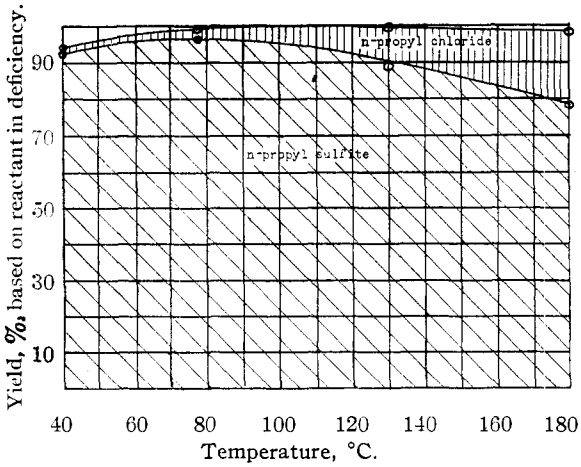


Fig. 5.—Yield of products from *n*-propyl alcohol as a function of temperature using a 2:1 ratio of alcohol to thionyl chloride.

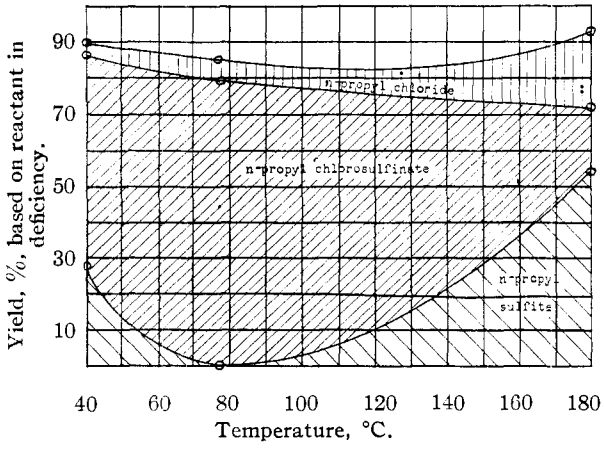


Fig. 6.—Yield of products from *n*-propyl alcohol as a function of temperature using a 1:2 ratio of alcohol to thionyl chloride.

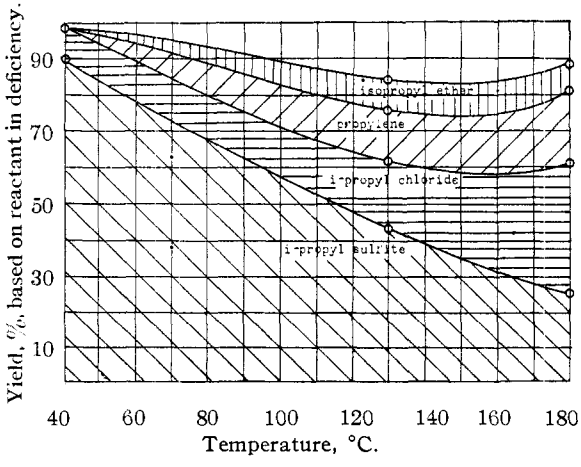


Fig. 7.—Yield of products from isopropyl alcohol as a function of temperature using a 2:1 ratio of alcohol to thionyl chloride.

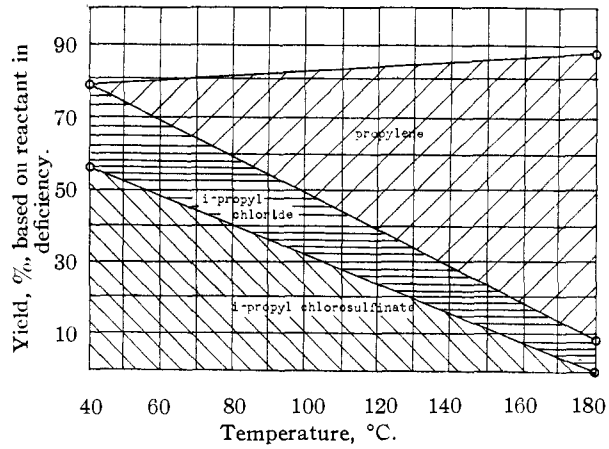


Fig. 8.—Yield of products from isopropyl alcohol as a function of temperature using a 1:2 ratio of alcohol to thionyl chloride.

alcohols were sulfite or chlorosulfinate esters (Figs. 5–8), the proportions dependent on the molar ratio used. Higher reaction temperatures decreased the yield of primary alkyl sulfite ester but slightly, while the yield of secondary alkyl sulfite ester was reduced from 90 to 26% as the temperature increased from 40 to 180°. Temperature had an even more pronounced effect on reducing the yields of alkyl chlorosulfinates. As the yields of esters decreased at the higher temperatures, the amounts of alkyl chlorides showed an increase, but this product was never obtained in large quantities from the primary or secondary alcohols. *t*-Butyl alcohol, on the other hand, was converted predominantly to alkyl chloride in all the reactions, regardless of temperature. That higher temperatures may alter the course of the reaction in some cases was strikingly illustrated from the results obtained with isopropyl alcohol. While the reaction of this alcohol with thionyl chloride at 40° gave chlorosulfinate, sulfite, and alkyl chloride, temperatures of 130 and 180° led to an entirely different type of reaction, *i. e.*, dehydration. Depending on the molar ratios used, the products were olefin and ether or olefin only. In the reactions at 130° and, especially, at 180°, the reactants were easily volatilized and considerable reaction may have occurred in the vapor phase.

Ratio of Reactants.—It will be noted (Figs. 1–4) that lower yields of sulfite esters resulted when the ratio of alcohol to thionyl chloride was above 2:1. The excess (100%) alcohol may have acted as a solvent for the hydrogen chloride thereby permitting reaction 7 to occur. This hypothesis was supported by the noticeable increases in *n*-propyl and isopropyl chloride yields which occurred when the ratio of alcohol to thionyl chloride was increased from 2:1 to 4:1. The use of excess (100%) thionyl chloride, on the other hand, did not seem to exert such significant influences.

The yields of chlorosulfinates reported are perhaps high in several experiments because the re-

action mixtures were allowed to stand overnight in the presence of the excess thionyl chloride before distillation. This permitted reaction 4 to occur, thereby increasing the chlorosulfinate yield at the expense of some sulfite. However, even with the use of a five-fold excess of thionyl chloride as the sole refluxing solvent it was not possible to form *n*-propyl chlorosulfinate exclusively, without some sulfite formation also taking place. If this reaction mixture was allowed to stand for sixteen hours at 25° before distillation, all sulfite was converted to chlorosulfinate. These results afford interesting information on the relative rates of reactions 1, 2 and 4. Libermann[7] has reported that reactions 1 and 2 are very rapid while reaction 4 is slow, although accelerated at elevated temperatures. Our results indicate that, at 78°, reaction 2 is considerably faster than 1, while reaction 4, for some reason not yet fully understood, does not appear important at this temperature but becomes prominent with longer contact times at room temperature. For example, in a series of three experiments, one mole of *n*-propyl alcohol was dropped into six moles of refluxing thionyl chloride in one hour, after which the mixture was refluxed for three or six hours before distillation. The yields of *n*-propyl sulfite were 30 and 32%, respectively, showing reaction 2 to be considerably faster than 1 at 78° and indicating that reaction 4 was unimportant. If reaction 1 was equally fast or faster than 2 at 78°, one would expect chlorosulfinate formation predominantly because of the large excess of thionyl chloride and the relatively small concentration of alcohol present at any time. In this connection, we[16] briefly investigated the reaction of *n*-butyl alcohol with a 100% molar excess of thionyl chloride at 0°, using no other solvent and making no effort to eliminate hydrogen chloride. After a four-hour reaction time at 0°, the thionyl chloride was removed under vacuum and distillation of the residue gave an 86% yield of *n*-butyl chlorosulfinate and no sulfite. Other workers[3,8] have obtained 70–80% yields of ethyl and isopropyl chlorosulfinates by somewhat similar experiments. These results indicate that reaction 1 is rapid even at 0°, whereas reaction 2 apparently becomes much slower at this lower temperature.

It is difficult to make any generalized statements about the effect of ratio of reactants on the yields of chlorides and olefins. With *n*-propyl alcohol, the yield of *n*-propyl chloride was not materially affected by changes in the ratio of reactants; with isopropyl alcohol, the alkyl chloride yield varied more pronouncedly, although a much more significant increase was observed in the olefin yield when the thionyl chloride concentration was increased. Thus, the propylene yield increased from 12 to 79% as the ratio of isopropyl alcohol to thionyl chloride at 180° was changed, from 4:1 to 1:2. In the tertiary alcohol reactions the ratio of reactants again seemed to have little effect on the olefin yield, which was small in all cases, but the yield of alkyl chloride varied greatly. These last yields are somewhat ambiguous, however, since *t*-butyl alcohol reacts so rapidly with hydrogen chloride.

Effect of Structure of Alcohol.—The primary and secondary alcohols formed sulfite esters in yields[17] of 90–96% whereas *t*-butyl sulfite could not be prepared, even at the low reaction temperature of 12°. The influence of the structure of the alcohol on altering the yields and types of products was more noticeable when excess thionyl chloride was used. Under such conditions, the formation of *n*-propyl chlorosulfinate proceeded in good yield (80%) but with the less stable isopropyl chlorosulfinate yields above 56% could not be obtained. No chlorosulfinate could be isolated from the reaction with *t*-butyl alcohol.

An added illustration of the effect of branching was in the observed fact that the primary alcohol underwent no dehydration in any of the reactions, while the secondary alcohol was converted to olefin in 79% yield and the tertiary alcohol was dehydrated to olefin in 22% yield, as a maximum.

Another distinguishing reaction of the secondary alcohol was that of ether formation, a previously unreported reaction for such systems. The mechanism involved in this ether formation is unknown but it appears significant that diisopropyl ether was formed only when the alcohol to thionyl chloride ratio was high. As partial evidence that the ether did not result from the thermal decomposition of isopropyl sulfite, a mixture of this ester and chlorobenzene was refluxed for four hours at 130° without producing any diisopropyl ether. Such reaction conditions had actually been used in one experiment where an 8% yield of ether was isolated. In addition, studies by Carré and Libermann[18] on the thermal stability of various sulfite esters showed that *n*-butyl sulfite can be refluxed at its boiling point (228°) without decomposition while *n*-decyl sulfite decomposed only at 310°, giving equal portions of decylene and decanol but no ether. The only examples of ether formation were obtained[18] from the pyrolysis of benzyl and 2-phenylethyl sulfites, where the presence of the phenyl group completely changed the course of the decomposition and gave high yields of ethers.

Acknowledgment.—We express our thanks to Dr. A. Pechukas, who suggested the refluxing solvent technique, and to Dr. F. Strain for helpful discussions.

Summary

1. The thermal stability of the propyl chlorosulfinates even at temperatures but slightly above normal was poor, with isopropyl chlorosul-

(16) Unpublished results of L. Summers of this Laboratory.

(17) Using this technique we have also prepared methyl sulfite (93% yield), ethyl sulfite (92%), *n*-butyl sulfite (86%), 2-chloroethyl sulfite (94%) and 2-cyanoethyl sulfite (88%).

(18) Carré and Libermann, *Bull. soc. chim.*, (5) **1**, 1248 (1934).

finate being considerably less stable than the *n*-propyl derivative.

2. As a previously undescribed reaction, it was found that alkyl sulfites reacted rapidly with hydrogen chloride forming alcohols and alkyl chlorides. This gas did not alter the rate of decomposition of alkyl chlorosulfinates.

3. Simultaneous addition to a refluxing solvent was found to be a convenient method for the reaction of primary and secondary alcohols with thionyl chloride to give sulfite and chlorosulfinate esters in good yields.

4. The variables of temperature, type of alcohol, and ratio of reactants have been studied in the reaction of alcohols with thionyl chloride in a refluxing solvent. The *primary* alcohol followed the expected metathesis, forming either sulfite or chlorosulfinate, depending on the molar ratio used At higher temperatures the chlorosulfinate yield decreased sharply, while olefin and alkyl chloride yields increased. The *secondary* alcohol gave an excellent yield of sulfite ester at low temperature but the chlorosulfinate yield was low and erratic under all conditions. At higher temperatures olefin or alkyl chloride formation predominated. The formation of diisopropyl ether represented a new type of reaction in which thionyl chloride was involved. The *tertiary* alcohol formed only alkyl chloride and olefin.

BARBERTON, OHIO RECEIVED APRIL 3, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF NEUROLOGY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY AND THE NEUROLOGICAL INSTITUTE]

Immunochemical Studies on Blood Groups. V. Further Characterization of Blood Group A and O Substances from Individual Hog Stomachs[1a]

BY AARON BENDICH,[1b] ELVIN A. KABAT AND ADA E. BEZER

Gastric mucin prepared from random pools of hog stomachs has been widely employed[1c-5] as a source of the blood group A substance, despite the observation of Witebsky[6] that not all hog stomach linings showed blood group A activity. In a recent study from this Laboratory[7] in which individual hog stomach linings were used, it was found that only seven of ten stomachs examined showed blood group A activity; the remaining three were inactive in this respect. By autolysis or peptic digestion and subsequent purification (*cf.* 4, 7) products were obtained from all ten stomachs in approximately the same yield which were identical, within experimental error, in nitrogen, glucosamine, reducing sugar and acetyl content, and in relative viscosity. They could only be distinguished by their immunological and quantitative immunochemical properties,[7] seven showing a capacity to inhibit the hemagglutination of A cells by human anti-A, to precipitate anti-A from sera of humans of blood groups B and O,[5] and to induce the formation of isoagglutinins for A erythrocytes on injection into man[8]; the purified materials from the remaining three hogs were inactive in these respects.[7]

By applying the methods of quantitative immunochemistry (for reviews *cf.* refs. 9, 10, 11), six of the seven active products were found to show equal potency in precipitating anti-A and on an average, eighty-four per cent. of the glucosamine of these preparations was specifically precipitable by excess anti-A (the seventh was somewhat less active). This latter finding provides strong evidence for the high degree of purity of the active preparations on an absolute basis.

Evidence has since been obtained[12,13] indicating that the inactive products show blood group O activity; the high degree of purity of these preparations has been adduced from a quantitative immunochemical study of the cross-reaction of both the A and inactive substances with Type XIV antipneumococcal horse serum.[13] The present communication presents data showing the inactive substances previously isolated to have blood group O activity and indicates that individual hog stomach linings may contain either A substance or O substance alone and that certain hogs' stomach linings contain both A and O substances in varying proportions. It also records several additional immunological, physical, and chemical properties of the purified A and O substances and the isolation of *d*-glucosamine and of derivatives of *l*-fucose and *d*-galactose from hydrolysates. The finding of *l*-fucose confirms and extends the

(1a) The work described in this paper was carried out under a grant-in-aid from the United States Public Health Service and in part under the William J. Matheson Commission.

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