695. *Experiments on the Interaction of Hydroxy-compounds and Phosphorus and Thionyl Halides in the Absence and in the Presence of Tertiary Bases. Part VII.*

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Velocities of decomposition of a number of chlorosulphinates, RO•SOCl, to the respective chloride, RCl, and sulphur dioxide in the presence of small amounts of pyridine hydrochloride have been determined at different temperatures. The results clearly show the time–temperature requirements for complete decomposition, information which has significance in the Darzens procedure.

Even when such small amounts as 0·01 mol. of base hydrochloride for each mol. of chlorosulphinate were used, the systems were physically heterogeneous, and stirring had a material influence on the rate of decomposition. Although specific rates calculated on the basis of a first- or second-order system showed considerable variations during each reaction, the base hydrochloride not being allowed for, the results provide useful guidance in further investigations into the mechanism of replacement of hydroxyl group by halogen.

In the study of Walden inversion reactions the readier replacement of the hydroxyl group by a chlorine atom by means of thionyl chloride in conjunction with pyridine (Darzens, *Compt. rend.*, 1911, **152**, 1314, 1601) has been of considerable interest, and the process appears to involve the formation, probably *via* the sulphite, $SO(OR)_2$, of the chlorosulphinate, RO•SOCl, and its decomposition (Frankland and Garner, *J.*, 1914, **105**, 1101; McKenzie and Clough, *J.*, 1913, **103**, 687; Levene and Mikeska, *J. Biol. Chem.*, 1924, **59**, 473; McKenzie and Tudhope, *ibid.*, 1924, **62**, 551; Kenyon, Phillips and co-workers, *Trans. Faraday Soc.*, 1930, **26**, 451; Gerrard, *J.*, 1936, 688; 1939, 99; 1940, 218; 1944, 85; Hughes, Ingold, and co-workers, *J.*, 1937, 1252). That pyridine facilitates these two processes, there is no doubt; that pyridine hydrochloride or pyridine itself facilitates the formation of the chlorosulphinate from the sulphite, has still to be decided. Gerrard (*loc. cit.*) showed that the interaction of the chlorosulphinate and pyridine itself presented very different phenomena from those presented by the chlorosulphinate–pyridine hydrochloride system. Furthermore, in reply to Libermann (*Nature*, 1947, **160**, 903; cf. Gerrard and French, *ibid.*, 1947, **159**, 263), it has been shown that there can be structural factors which render the employment of pyridine not merely unnecessary, but, from the point of view of yield of chloride, RCl, undesirable. An excellent yield of 1-chloro-1-phenylethane is readily obtained by mixing the alcohol and thionyl chloride; but no evidence has yet been secured to show that the chlorosulphinate is an intermediate. Even in the presence of pyridine at −10°, chloride, RCl, is formed during the actual addition of thionyl chloride; but the yield of chloride is considerably reduced.

Carrè and Libermann (*Bull. Soc. chim.*, 1933, **53**, 1051) manometrically determined the temperature at which sulphur dioxide was evolved from an equimolecular mixture of a certain alcohol, pyridine, and thionyl chloride. Such a temperature was referred to as the temperature of decomposition of the respective chlorosulphinate " in the presence of pyridine." It does not follow, however, that the temperature at which the sulphur dioxide disentangled itself in an appreciable amount from the reaction mixture was that at which its formation became measurable. Furthermore, the temperature might have been that at which the interaction of the thionyl chloride and sulphite became appreciable, the chlorosulphinate then undergoing rapid decomposition.

The present investigation is a step towards a more detailed study of the thionyl chloride–hydroxy-compound system, and concerns the determination of the rates of decomposition of a number of chlorosulphinates in the presence of small amounts of pyridine hydrochloride at different temperatures. The outstanding feature is the determination, with serviceable precision, of the time–temperature factor, which refers to the time for which the system must be heated at a given temperature to effect a stated percentage decomposition of the chlorosulphinate. To illustrate the significance of this information we refer to the experiment of Whitmore and Rothrock (*J. Amer. Chem. Soc.*, 1932, **54**, 3431) in which *neo*pentyl alcohol, pyridine, and thionyl chloride were mixed in ethereal solution at 0°. There is no mention that the mixture was warmed; after 24 hours the mixture was worked up in the usual way. Of the original alcohol, 75% was recovered, and no chloride, RCl, was isolated. It is now clear that any resistance to replacement of the hydroxyl group by chlorine was not seriously challenged in this experiment, even though, as Whitmore and Rothrock stated, the procedure was " the method of Darzens," modified until it gave over 30% yields of 1-chlorobutane from butan-1-ol.

In the experimental part we present a selection from all the data we accumulated in order to illustrate the general trend of the phenomena. We purposely avoided any serious deviation from the conditions usually prevailing during the application of the Darzens procedure. The conclusions we draw at this stage are that decomposition is occurring not only by the catalytic influence of the pyridine hydrochloride dissolved in the chlorosulphinate, but also by its influence on the chlorosulphinate dissolved in the molten pyridine hydrochloride. Diffusion of chloride, RCl, out of, and of the chlorosulphinate into, the latter will be significant. The availability of base hydrochloride dissolved in the reaction liquid will vary, not merely because of the decrease in concentration of the chlorosulphinate, but also because of the variation in solubility of the hydrochloride as the liquid changes from 100% chlorosulphinate to 100% chloride.

EXPERIMENTAL.

The chlorosulphinate and base hydrochloride were contained in a vessel fitted with a mechanical stirrer, an exit tube which passed through an upright condenser, and another exit tube which passed to the bottom of the reaction vessel, but was slightly turned up at the bottom to ensure that the end of the tube was clear of the pool of molten pyridine hydrochloride. To the outside end of this exit tube was attached a small sampling bulb, of known volume, furnished with a tap at each end. The other exit tube which passed through the condenser was attached to a pair of levelling tubes containing dry air over mercury. By manipulation of the levelling tubes pressure was applied to the surface of the reaction liquid, and some of the latter was thereby forced up into the sampling bulb. The sample was rapidly transferred to an appropriate amount of an aqueous solution of sodium hydroxide in a bottle which was immediately stoppered, and shaken. By the method of Volhard, the chloride-ion content, indicating unchanged chlorosulphinate, was determined. When an attempt was made to withdraw a sample by reducing pressure in the sampling bulb, bubbles of sulphur dioxide confused the operation. Temperature control was by a gas-thermoregulator, and the thermostat-bath liquid was an oil which was well stirred.

FIG. 1.

Effect of quantity of pyridine hydrochloride on rate of decomposition of iso*amyl chlorosulphinate: unstirred conditions.*

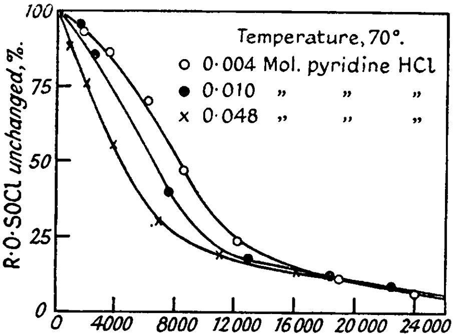


FIG. 2.

Comparison of rates of decomposition of iso*amyl chlorosulphinate in the presence of the hydrochlorides of tertiary bases:* 80°, *unstirred.*

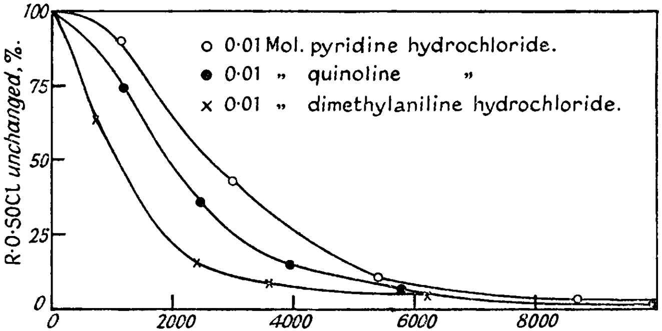
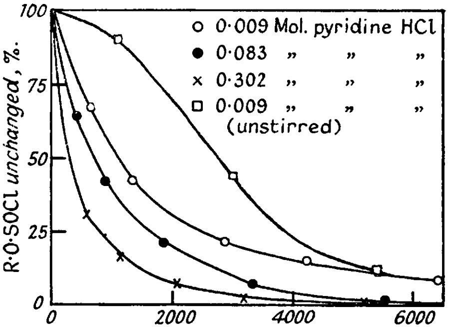


FIG. 3.

Effect of quantity of pyridine hydrochloride on rate of decomposition of iso*amyl chlorosulphinate:* 80°, *stirred.*



In Fig. 1 is shown the effect of the change in amount of pyridine hydrochloride, the system being unstirred at 70°. The curves for 80° are steeper, and decomposition was almost complete at the end of 2 hours. In Fig. 2 the influence of a change in tertiary base hydrochloride is shown, the amount of respective hydrochloride being 0·01 mol. The system was unstirred. Fig. 3 illustrates data obtained for different amounts of pyridine hydrochloride, the system being stirred. One curve for 0·009 mol. of the hydrochloride, the system being unstirred, is shown in contrast. When 0·3 mol. of hydrochloride was used at 80°, 90% of the *iso*amyl chlorosulphinate was decomposed in 30 minutes. Fig. 4 illustrates the influence of temperature on the rate of decomposition of *n*-butyl chlorosulphinate. Data from similar curves are expressed as percentage decomposition after 2000, 4000, 6000, and 8000 secs. for *iso*amyl chlorosulphinate at 40° (4, 7, 11, 14%), 50° (7, 11, 15, 18%), and 70° (38, 58, 71, 80%), for 1-chloro-2-chlorosulphinoxyethane at 40° (1, 2, 2·5, 3%), 50° (3, 5, 7, 9%), 60° (16, 27, 36, 42%), and 70° (28, 52, 70, 81%), and for ethyl α-chlorosulphinoxypropionate at 30° (3, 6, 9, 10·5), 40° (7·5, 14, 20, 25%), 50° (12·5, 21, 27, 31%), and 60° (33, 52·5, 65·5, 76%). The reaction mixture was rapidly stirred and 0·01 mol. of pyridine hydrochloride was used.

FIG. 4.

Decomposition of n-*butyl chlorosulphinate in presence of* 0·01 *mol. of pyridine hydrochloride.*

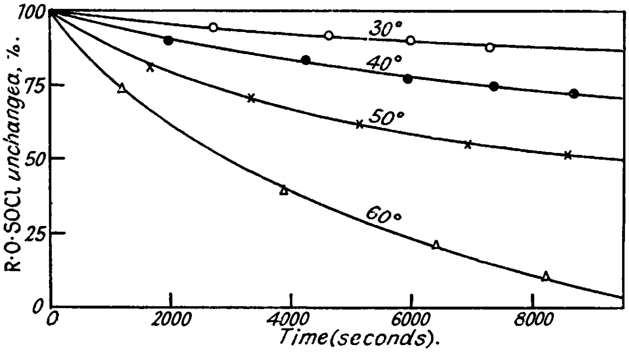
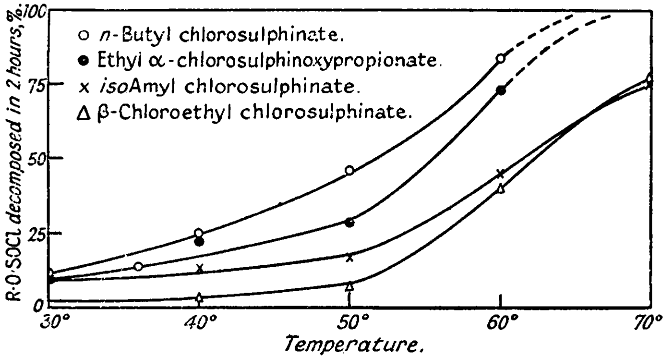


FIG. 5.

Effect of temperature on chlorosulphinate decomposed (%) *in* 2 *hours in the presence of* 0·01 *mol. of pyridine hydrochloride.*



To illustrate the variation in specific rate of first-order and second-order reactions with respect to the concentration of *iso*amyl chlorosulphinate at 60° and for 0·01 mol. of pyridine hydrochloride, data are given in the following table. The system was rapidly stirred.

Time of reaction, secs.	RO·SOCl, unchanged, %.	Concn. of RO·SOCl, g.-mol./l.	10^5k_1.	10^5k_2.	Time of reaction, secs.	RO·SOCl, unchanged, %.	Concn. of RO·SOCl, g.-mol./l.	10^5k_1.	10^5k_2.
0	100	6·14	—	—	5,520	62·2	3·82	8·60	1·79
600	94·5	5·80	9·52	1·59	7,680	53·8	3·30	8·09	1·82
1620	84·6	5·19	10·40	1·84	9,900	45·6	2·80	7·93	1·96
3360	73·0	4·48	9·38	1·80	11,150	40·4	2·48	8·13	2·16

In Fig. 5 the amounts of chlorosulphinate decomposed in 2 hours are plotted against the temperature. The curves for the chlorosulphinates, RO·SOCl where R = *n*-C_4H_9, CH_3·CH·CO_2Et, *iso*-C_5H_{11}, and CH_2Cl·CH_2 are compared. It is clear that the curves do not strike the temperature axis abruptly.

Equimolecular quantities of thionyl chloride, pyridine, and hydroxy-compound were mixed at −10° as described by Carré and Libermann. Such mixtures were heated in a thermostatically controlled bath at temperatures below those quoted by these workers as " decomposition temperatures." Each mixture was in turn treated with ice, and the chloride ion determined by the Volhard method, allowance being made for the permanent presence of 1 g.-ion proportion of chlorine. The percentage loss of chloride ion is stated with respect to the hydroxy-compound in the system, the respective mixture having been heated for 1 hour : Ethyl lactate (30°) (40%), butan-1-ol (40°) (43%), 2-chloroethan-1-ol (40°) (73%).

Two parallel experiments were conducted with *iso*amyl chlorosulphinate. In one, this substance (1 mol.) was kept in contact with 0·01 mol. of pyridine hydrochloride in a stoppered bottle at 20—25° for 48 hours. On the bottle being opened, it was noticed that a pressure had developed, and there was a strong smell of sulphur dioxide. Analysis showed that 15·4% of the original chlorosulphinate had decomposed. In the other experiment, the base hydrochloride was omitted, and it was found that the chlorosulphinate could be kept for weeks without the occurrence of appreciable decomposition. From time to time it has been noticed that certain batches of butan-1-ol, even after normal purification by distillation, could not be successfully converted into the distilled chlorosulphinate. Decomposition always occurred during distillation. However, after such a specimen of alcohol had been washed with dilute sulphuric acid, then washed free from acid, and dried, a distilled specimen of chlorosulphinate could then be obtained from it. We attribute this behaviour to the presence of traces of tertiary base in the alcohol, and we attach some importance to such small amounts of tertiary base which might adventitiously find their way into the materials and apparatus, from the laboratory atmosphere in which tertiary bases may recently have been handled.

Neither glass wool, nor silica gel, nor powdered potassium chloride, all carefully dried, encouraged the decomposition of ethyl α-chlorosulphinoxypropionate at temperatures below 150°, the temperature at which the chlorosulphinate decomposed when alone. When pyridine hydrochloride (0·017—0·32 mol. per mol. of chlorosulphinate) was used the temperature at which the evolution of sulphur dioxide was *obvious* was about 47°, and coincided with the melting of the hydrochloride. The bubbles of sulphur dioxide were noticed only at the liquid–liquid interface.

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