[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics and Mechanism of the Reaction between Thionyl Chloride and Dibutyl Sulfite

BY PAUL D. BARTLETT AND HARRY F. HERBRANDSON[1]

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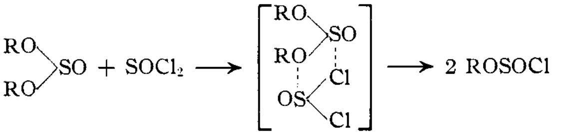
The reaction between di-*n*-butyl sulfite and thionyl chloride yields *n*-butyl chlorosulfinate. The reaction is nearly enough irreversible to be treated kinetically as such. A kinetic study of the reaction in nitrobenzene as solvent shows that the reaction is not a simple second order metathesis between the two reactants. When the two reactants are present at equal concentrations, the rate is proportional to the concentration of one reactant and the kinetics is plainly of the first order. When the reactants are present at unequal concentrations, the reaction is roughly of the first order with respect to dibutyl sulfite and not even approximately so with respect to thionyl chloride. The reaction is powerfully catalyzed by chloride ion introduced in the form of benzylpyridinium chloride of concentrations of the order of 10^{-4} to 10^{-3} *M*, but not by hydrogen chloride at similar concentrations. These are the properties to be expected of an ionic chain reaction involving the steps: $Bu_2SO_3 + Cl^- \rightarrow BuOSOCl + BuO^-$ (1); $SOCl_2 + BuO^- \rightarrow BuOSOCl + Cl^-$ (2).

Introduction

The preparation of a primary alkyl chlorosulfinate takes a peculiar course.[2,3] Although the chlorosulfinate is presumably an intermediate in the formation of the dialkyl sulfite from the alcohol and thionyl chloride

$$ROH + SOCl_2 \longrightarrow HCl + ROSOCl$$
$$ROH + ROSOCl \longrightarrow HCl + (RO)_2SO$$

the second step follows so closely after the first that only dialkyl sulfite can be isolated at an early stage of the reaction. Subsequently, however, a reaction between dialkyl sulfite and thionyl chloride takes place producing eventually a good yield of alkyl chlorosulfinate. The latter reaction has been formulated[3] as a direct metathetical process occurring between one molecule of dialkyl sulfite and one of thionyl chloride.



So many apparently bimolecular metathetical reactions have been shown upon kinetic investigation not to belong to this type that the present reaction has seemed to merit a careful kinetic examination. We have found that indeed the kinetics is incompatible with a direct bimolecular reaction of the type postulated.

Experimental

The example chosen for study was the reaction of di-*n*-butyl sulfite with thionyl chloride in nitrobenzene as a solvent at 25°. Under these conditions, using ordinary reagents, the reaction was almost too fast to measure. However, successive improvements in the purification of the solvent and in the technique of carrying out the reaction brought about a steady decrease in the rate of reaction. Eventually it was found that pure dibutyl sulfite and pure thionyl chloride failed to react in nitrobenzene at 25° in any reasonable length of time. This extreme reduction in the rate of reaction was found to be due to the removal of impurities causing the production of small amounts of chloride ion.

Reagents.—Nitrobenzene, purchased from the Eastman Kodak Co., was steam distilled from dilute sulfuric acid, washed with water and dried over calcium chloride. Distilled at atmospheric pressure, it boiled over a 1° range. It had a refractive index $n^{25}\mathrm{D}$ 1.5500. *n*-Butyl alcohol was dried over potassium carbonate and then distilled through a Lecky–Ewell column[4] of 60 theoretical plates. It had a boiling point of 116°, $n^{25}\mathrm{D}$ 1.3980. The thionyl chloride and dibutyl sulfite were provided by the Columbia Chemical Division of the Pittsburgh Plate Glass Co. (now the Columbia-Southern Chemical Corp.) and were used without purification. *n*-Butyl chlorosulfinate for the experiments on the analytical method was prepared as follows: To 182 cc. (2.5 moles) of purified thionyl chloride in a 500-cc. flask fitted with a stirrer, dropping funnel and exit tube was added with cooling 183 cc. (2 moles) of *n*-butyl alcohol. The solution was allowed to warm gradually to room temperature and after a few days it was distilled under diminished pressure. After 46 g. of forerun had been collected, 270 g. (1.73 moles, 86%) of butyl chlorosulfinate,[3] $n^{25}\mathrm{D}$ 1.4572, distilled at 53.5° (9.5 mm.).

Analytical Method.—The analytical method chosen was based upon the fact that thionyl chloride reacts with anhydrous formic acid to produce a mole of carbon monoxide, whereas neither dibutyl sulfite nor butyl chlorosulfinate produces any carbon monoxide.[2,3] The apparatus for the analysis consisted of a 50-cc. flask with a standard taper joint fitted with an adapter permitting the use of a mechanical stirrer and an inlet and outlet tube. The air in the flask was displaced with carbon dioxide which was used to sweep the evolved gases through a gas-washing bottle containing 28% potassium carbonate solution into a 100-cc. nitrometer containing 50% potassium hydroxide. The analytical flask originally contained 10 cc. of anhydrous formic acid. Into it through a rubber stopper 1-cc. solutions of thionyl chloride in benzene or nitrobenzene were introduced from a hypodermic syringe. The gases from the analysis were swept through the apparatus with pure carbon dioxide until only micro bubbles rose in the nitrometer. The volume of the carbon monoxide was measured and corrected in the usual manner. The Henry's law absorption coefficient of carbon monoxide in 50% potassium hydroxide solution at 26° was found to be 0.032, corresponding to the absorption of 0.80 cc. of carbon monoxide in 24.74 cc. of 50% potassium hydroxide solution.

It was found that no carbon monoxide was evolved by dibutyl sulfite nor by butyl chlorosulfinate. The evolution of carbon monoxide by thionyl chloride was not quantitative but was reproducible, and with a set of corrections established by determinations of known samples it was possible to make the method a reliable one for analysis.

Kinetic Method.—The kinetic determinations were carried out in a two-bulb flask with an attached tube through which a small positive pressure of dry carbon dioxide could be applied. In a typical run 25 cc. of a 0.256 *M* solution of dibutyl sulfite in nitrobenzene was added initially to one bulb. To the other was added 25 cc. of a 0.275 *M* solution of thionyl chloride in the same solvent. The flask was closed with a rubber stopper and immersed in a 25° thermostat for about 30 minutes. The solutions were then mixed by upending the flask in the thermostat and shaking well. At successive times 5-cc. samples of the reactant solution were withdrawn through the rubber stopper by means of a hypodermic needle. These were introduced into the analytical apparatus and the volume of carbon monoxide was determined.

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[1] This work was done while the junior author was a Pittsburgh Plate Glass Fellow at Harvard University in 1947.

[2] P. Carré and D. Libermann, *Bull. soc. chim.*, **53**, 1050 (1933).

[3] W. Gerrard, *J. Chem. Soc.*, 99 (1939).

[4] H. S. Lecky and R. H. Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

Another method of analysis also reported by Carré and Libermann was investigated and found to be quite precise. This is the reaction of thionyl chloride with pyridine oxalate. The method, however, is not applicable to our present problem since both thionyl chloride and butyl chlorosulfinate liberate carbon monoxide apparently quantitatively and the method will therefore not distinguish between them.

There was no direct way of determining the concentrations of dibutyl sulfite. These were therefore determined during any run on the assumption that a constant difference existed between the concentrations of thionyl chloride and of dibutyl sulfite throughout the run. This constant difference was established by the determination of the initial concentrations of the reactants. It was found that the lone initial concentration of thionyl chloride did not usually yield a point which fell on the line joining the other experimental points during a run and more consistent results were obtained by taking an extrapolated value for the initial concentration of thionyl chloride. This difficulty, not uncommon in kinetic work, is probably the result of the fact that mixing is never an instantaneous process and zero time kinetically does not correspond exactly to the moment of shaking the reagents together in the flask. As a check upon the calculated initial concentration of dibutyl sulfite it was possible to perform an indirect determination using thionyl chloride in excess as the reagent and accelerating the reaction between dibutyl sulfite and thionyl chloride (see below) by the addition of a substantial concentration of benzylpyridinium chloride. In a typical experiment the concentration of dibutyl sulfite estimated by the total thionyl chloride consumed was 0.247 *M*, while the calculated concentration from the amounts of dibutyl sulfite and nitrobenzene initially taken was 0.254 *M*. The experimentally determined figure was taken as the basis for establishing the concentrations in the runs.

The solutions of benzylpyridinium chloride and of hydrogen chloride in nitrobenzene were made up and titrated by the Volhard method, being then used as stock solutions to produce the desired concentrations in the solutions used for kinetic analysis.

Results

Table I shows a typical set of kinetic data for one of the early runs between thionyl chloride and dibutyl sulfite without known addition of chloride ion. The fact that this reaction took place at all must have been due, as discovered later, to the accidental presence of a minute amount of chloride ion. The results are valid, however, to the extent that they show that the reaction does not have the kinetic properties typical of a bimolecular metathesis. Figure 1 shows the data plotted for a bimolecular reaction and also for a first order reaction of dibutyl sulfite.

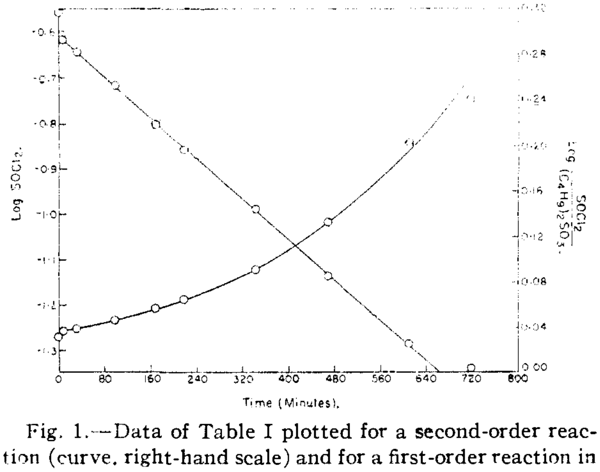

Fig. 1.—Data of Table I plotted for a second-order reaction (curve, right-hand scale) and for a first-order reaction in dibutyl sulfite or thionyl chloride (line, left-hand scale).

The experiments summarized in Table II bring out some striking facts with regard to this reaction. Chief among these is the role of chloride ion. In the runs without any chloride added no detectable change had taken place in the concentration of thionyl chloride after 147 minutes in the presence or absence of hydrogen chloride. In the presence of benzylpyridinium chloride at a concentration of 0.0016 *M* the reaction was apparently 100% complete in this same length of time. At intermediate concentrations the effect of chloride ion upon the rate of reaction was as indicated in Table II. In the table the quantity *ka* represents the experimental first order rate constant based upon dibutyl sulfite and *k* represents this rate constant divided by the initial concentration of benzylpyridinium chloride. It is seen that within reasonable limits, despite the enormous range of rates observed, the rate is proportional to the concentration of benzylpyridinium chloride. The lack of effect of hydrogen chloride on the rate is shown in the last three lines of the table. No reaction is observed in the presence of hydrogen chloride and in the absence of benzylpyridinium chloride. When both were present the rate was indistinguishable from that observed with the same concentration of benzylpyridinium chloride but in the absence of hydrogen chloride.

TABLE I

REACTION OF THIONYL CHLORIDE WITH DIBUTYL SULFITE IN NITROBENZENE AT 25°

Time, min.	Thionyl chloride, mole per liter	Dibutyl sulfite, mole per liter	Reaction, %
0	0.275 (calcd.)	0.256 (calcd.)	0
7	.241	.222	13
32	.226	.207	19
98	.192	.172	33
168	.158	.139	46
218	.129	.120	53
343	.103	.083	68
468	.073	.054	79
609	.052	.032	87
717	.046	.026	90

TABLE II

SUMMARY OF RATE CONSTANTS

Initial chloride, mole per liter	Initial sulfite, mole per liter	Initial thionyl chloride, mole per liter	Obs. first order rate constant, *ka*, sec.$^{-1}$	*k*, l./mole sec.
0.000218	0.247	0.254	0.0000829	0.380
.000316	.247	.252	.0000986	.312
.000435	.247	.256	.000136	.312
.000644	.247	.256	.000196	.204
.000870	.247	.246	.000257	.295
.000870	.247	.252	.000270	.310
.000218	.247	.480	.0000702	.223
.000218	.247	.495	.0000876	.403
.000322	.098	.516	.000103	.320
.000435	.247	.122	.000136	.312
.000218	.494	.235	.0000741	.340
.0[a]	.247	.258	.0	.0
.000322[a]	.247	.252	.0000940	.292
			Average	.325

[a] 0.000512 *M* in hydrogen chloride.

Clean first-order kinetics was observed only in those runs in which the concentration of dibutyl sulfite was approximately equal to that of thionyl chloride. In these runs it is impossible to determine whether the reaction was of the first order with respect to the one reactant or to the other. All the other runs, however, present a semblance of a linear relation between the logarithm of the concentration of dibutyl sulfite and time, whereas there is no such relationship between time and the logarithm of the thionyl chloride concentration.

Interpretation of the Kinetic Data

These facts definitely exclude the one-step molecular metathetical mechanism. A reaction by such a mechanism would be of the second order and it would offer no visible role for chloride ion in promoting the reaction and indeed in being a seemingly essential part of it. The importance of chloride ion in the reaction suggests that the process is a stepwise one, perhaps initiated by an attack of chloride ion upon dibutyl sulfite and carried on in a manner resembling familiar chain reactions but with the chain carriers being ionic in character and incapable of combination with one another. Such a series of reactions might be

$$Bu_2SO_3 + Cl^- \xrightarrow{k_1} BuOSOCl + BuO^- \qquad (1)$$

$$SOCl_2 + BuO^- \xrightarrow{k_2} BuOSOCl + Cl^- \qquad (2)$$

If it is assumed that equations (1) and (2) represent the only mode of escape for either chloride or butoxide ion, then

$$(Cl^-) + (BuO^-) = a;\ (BuO^-) = a - (Cl^-)$$

where a is a constant equal to the initial concentration of chloride ion. If the initial concentrations of butyl sulfite and thionyl chloride are very much greater than the chloride ion concentration, the steady-state approximation can be made. Then if

$$(SOCl_2) = x$$

$$(Bu_2SO_3) = x + c$$

$$k_1(Cl^-)(x + c) = k_2x[a - (Cl^-)]$$

Solving for (Cl^-), we have

$$(Cl^-) = \frac{k_2ax}{k_2x + k_1(x + c)}$$

Through the rate of either reaction (1) or reaction (2) we then arrive at the over-all rate equation

$$\frac{-dx}{dt} = k_1(x + c)(Cl^-) = \frac{k_1k_2ax(x + c)}{k_2x + k_1(x + c)} \qquad (3)$$

Equation (3) has the property of reducing to a first-order kinetic equation in $(x + c)$ if $k_2 \gg k_1$ or if $c = 0$, and to a first-order kinetic equation in x if $k_1 \gg k_2$ or if $c = 0$. Plots of log x against time show clearly that the condition $k_1 \gg k_2$ does not apply, for the disappearance of *thionyl chloride* (x) is of first order only when the sulfite and thionyl chloride concentrations are initially equal, *i.e.*, when $c = 0$. In this case the rate equation is

$$\frac{-dx}{dt} = \frac{k_1k_2a}{k_1 + k_2}\, x$$

and the rate is expected to be directly proportional to a, the initial concentration of chloride ion. This is just what is observed. In the experiments with unequal concentrations of sulfite and thionyl chloride log $(x + c)$ is a roughly linear function of time, and it appears that k_1 is less than k_2, but probably not negligible compared to it. The pseudo first-order rate constants of column 4 of Table II vary with the chloride ion concentration as would be expected from equation (4); the figures obtained in column 5 by dividing the rate constant by the chloride concentrations are a true constant, equal to $k_1k_2/(k_1 + k_2)$, which we shall call k. The average value of this constant is 0.32 l./mole sec. The larger k_2/k_1, the more nearly k approaches k_1.

Without any assumption regarding the relative magnitudes of k_1 and k_2, equation (3) can be integrated to

$$\ln \frac{x_0 + c}{x + c} + \frac{k_1}{k_2} \ln \frac{x_0}{x} = ak_1t \qquad (4)$$

The two runs in which the sulfite concentration was substantially greater than the thionyl chloride concentration are fitted better by equation (4), with k_1/k_2 assumed to be equal to 0.2, than by the simple first order equation in $(x + c)$ (Figs. 2, 3). The runs in which the thionyl chloride concentration exceeds that of butyl sulfite are not improved by this treatment; their roughness probably derives from the fact that the thionyl chloride, which is the reactant determined quantitatively, is changing its concentration by a smaller fractional amount than in the other runs. The basis of selection of the value $k_1/k_2 = 0.2$ is shown in Fig. 2.

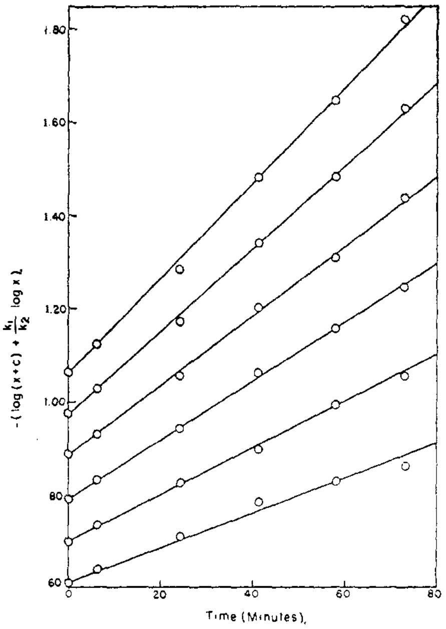

Fig. 2.—Data of a kinetic run (line 10 in Table II) plotted according to equation 4 with different assumed values of k_1/k_2, as follows: reading from the bottom line to the top, k_1/k_2 = 0, 0.1, 0.2, 0.3, 0.4, 0.5.

Although the kinetic characteristics of this reaction are those predicted by the above ionic chain mechanism, it is only with reluctance that we adopt a mechanism whereby butoxide ion is generated by the reaction of chloride ion with a sulfite and plays an essential recurring role in a reaction in the presence of thionyl chloride. Alternative formulations may be explored which involve

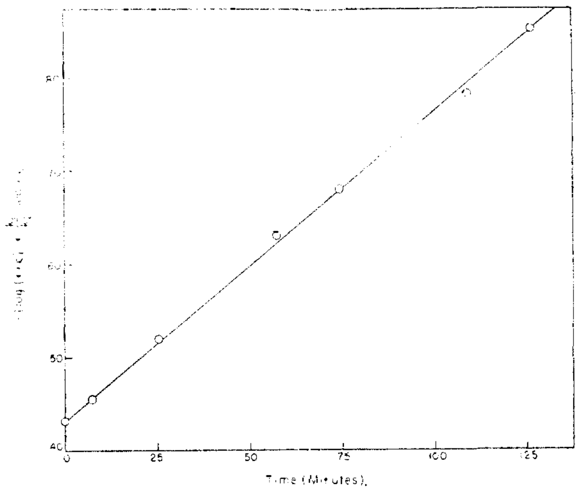

Fig. 3.—Data of a kinetic run (line 11 of Table II) plotted according to equation 4 with k_1/k_2 assumed equal to 0.2.

ionic chains but which do not require the presence of such an uncongenial fragment as a butoxide ion in the medium in which this reaction is occurring. One possibility which has been examined kinetically is

$$(\mathrm{BuO})_2\mathrm{SO} + \mathrm{Cl}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [(\mathrm{BuO})_2\mathrm{SOCl}]^- \qquad (5)$$

$$[(\mathrm{BuO})_2\mathrm{SOCl}]^- + \mathrm{SOCl}_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{BuOSOCl} + [\mathrm{BuOSOCl}_2]^- \qquad (6)$$

$$[\mathrm{BuOSOCl}_2]^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{BuOSOCl} + \mathrm{Cl}^- \qquad (7)$$

The essential feature of this mechanism is the hypothesis that when a chloride ion reacts with butyl sulfite it does not eject a butoxide ion but rather attaches itself with expansion of the valence shell of the sulfur to give a single new ion related to the butyl sulfite in somewhat the same way as the cyanhydrin anion is related to an aldehyde or a ketone. Any mechanism of this type runs into a difficulty which makes it appear even less attractive than the formulation which postulates the butoxide ion. The ion $[(\mathrm{BuO})_2\mathrm{SOCl}]^-$ can scarcely be very stable relative to the chloride ion and dibutyl sulfite from which it is formed, for its sulfur atom is in a state usually formed with difficulty. It does not seem at all likely that reaction (6) should be highly favored over a reversal of reaction (5) as a means of decomposition of this ion. If indeed reaction (5) is relatively rapidly reversed, then the ion $[(\mathrm{BuO})_2\mathrm{SOCl}]^-$ approaches equilibrium with its components, reaction (6) becomes rate-determining, and the process is a third order reaction in sulfite, chloride ion, and thionyl chloride. Only by having the initial complex ion decompose almost *entirely* by collision with thionyl chloride can the mechanism of equations (5–7) be capable of yielding the correct kinetics. These considerations do not, of course, exclude reaction (5) as a step in the accomplishment of reaction (1).

In a non-aqueous medium it may be a little surprising that an electrolyte such as benzylpyridinium chloride behaves kinetically as if it were a free chloride ion, especially since conductimetrically quaternary ammonium salts do not behave like ideal solutes in nitrobenzene.[5,6] It may be that the conducting chloride ions and the non-conducting ion pairs have very nearly the same ability to react as chloride ions or chloride ion donors with dibutyl sulfite. On the other hand, it is known that hydrogen chloride in nitrobenzene is very slightly ionized and in non-conducting form exists not as ion pairs but as covalent molecules.[7,8]

In any more basic solvent, or in the presence of water or an alcohol or ether, hydrogen chloride might be a sufficiently strong electrolyte to promote the reaction, and this may account for the lack of previous recognition of the catalytic nature of the reaction.

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CAMBRIDGE, MASSACHUSETTS

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