

Organic Sulfur Compounds. II. The Formation and Thermal Decomposition of Carboxylic Sulfurous Anhydrides

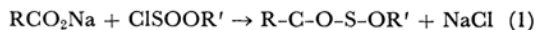
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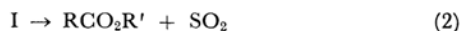
(Received November 1, 1965)

Mixed anhydrides of carboxylic acids and monoalkyl sulfites have been prepared, and their thermal decomposition has been studied. Some of these mixed anhydrides can be distilled without decomposition. Disproportionation to carboxylic anhydride and dialkyl sulfite is the main pathway of the thermal decomposition.

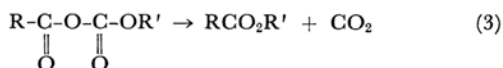
A mixed anhydride of carboxylic acid and sulfurous acid (I) has been postulated as an intermediate in the reaction of carboxylic acid salts and chlorosulfites to form the carboxylic esters,¹⁻³⁾ but it has not been isolated or identified. The formation of the carboxylic esters by the above method has been thought to proceed by the following reaction sequence:



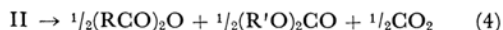
(I)



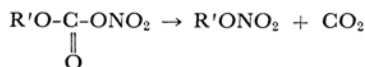
In the analogous decomposition of carboxylic carbonic anhydride (II),⁴⁾ the disproportionation reaction 4 takes place along with the reaction 3, which has a formal similarity to the reaction 2:



(II)



On the other hand, the nitric ester formation is the sole decomposition mode in the pyrolysis of the nitric carbonic anhydride (alkyl nitratocarbonate) (III):⁵⁾



(III)

In the present paper, the preparation of several compounds of this little known class of carboxylic sulfurous anhydride and studies of their reactions, including thermal decomposition, will be described.

Results and Discussion

Methyl chlorosulfite was found to react with the anhydrous sodium acetate to give methyl acetoxysulfinate (Ia) (I: R=R'=CH₃) as a colorless mobile liquid which can be distilled without decomposition in vacuo. This anhydride is extremely sensitive to moisture, by which it is decomposed to acetic acid and sulfur dioxide. The determination of sulfur by oxidation with hydrogen peroxide as barium sulfate indicated the presence of approximately the calculated amount of sulfur atoms in this compound. Its infrared spectrum exhibited a strong carbonyl band at 1757 cm⁻¹ which disappeared in contact with moisture, to be replaced by the absorption of acetic acid at 1712 cm⁻¹.

In a similar manner, ethyl acetoxysulfinate (Ib) (I: R=CH₃, R'=C₂H₅) was prepared from ethyl chlorosulfite and sodium acetate. The observed value of the sulfur content was close to the calculated figure. The high sensitivity of these anhydrides to moisture made the analysis very difficult. In the infrared spectrum, a strong carbonyl band at 1752 cm⁻¹ and a S-O stretching band at 1190 cm⁻¹ were observed.

Both the methyl ester and the ethyl ester were rather more stable than expected; they could be stored in a refrigerator for several days without any appreciable decomposition, provided strict caution was taken to avoid moisture.

The carbon tetrachloride solution of Ib was also stable; no change of its infrared spectrum was observed after one day. When refluxed for several hours, this solution produced acetic anhydride and ethyl sulfite, while it produced ethyl acetate on prolonged boiling. There was estimated to be a 40% decomposition in 3 hr. and a 55% decomposition in 6 hr.

When triethylamine was added to a solution of

1) P. Carré and D. Liberman, *Bull. soc. chim. France*, [4] 53, 1050 (1933).

2) M. S. Newman and W. S. Fones, *J. Am. Chem. Soc.*, 69, 1046 (1946).

3) M. S. Newman and C. Courduvelis, *J. Am. Chem. Soc.*, 86, 2942 (1964).

4) a) T. B. Windholz, *J. Org. Chem.*, 23, 2044 (1958); 25, 1703 (1960); b) D. S. Tarbell and F. J. Longosz, *ibid.*, 24, 774 (1959); c) F. J. Longosz and D. S. Tarbell, *ibid.*, 26, 2161 (1961); d) C. J. Michejda, D. S. Tarbell and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 84, 4113 (1962); e) C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, 29, 1168 (1964).

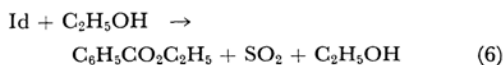
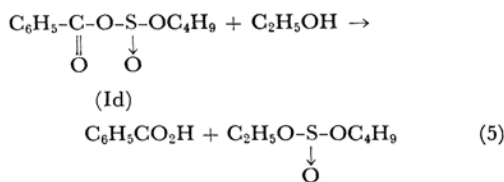
5) R. Boschan, *J. Am. Chem. Soc.*, 81, 3341 (1959); G. A. Mortimer, *J. Org. Chem.*, 27, 1876 (1962); D. N. Kevill and G. H. Johnson, *J. Am. Chem. Soc.*, 87, 928 (1965).

benzoic acid and ethyl chlorosulfite in carbon tetrachloride, an exothermic reaction took place, with the precipitation of triethylamine hydrochloride. The filtered solution showed strong infrared absorptions at 1724 cm^{-1} ($\text{C}=\text{O}$) and at 1222 cm^{-1} ($\text{S}-\text{O}$) (Fig. 1). The concentration of this solution under reduced pressure gave a pale sirup. The infrared spectrum of this liquid was the same as that of the carbon tetrachloride solution, suggesting the formation of ethyl benzoyloxysulfinate (Ic) ($\text{I: R}=\text{C}_6\text{H}_5$, $\text{R}'=\text{C}_2\text{H}_5$). This compound was also very sensitive to moisture, which caused its decomposition to benzoic acid.

The reaction mixture of sodium benzoate and ethyl chlorosulfite was extracted with carbon tetrachloride after the initial vigorous reaction had finished, and the insoluble powder was then filtered off. The infrared spectrum of the filtrate was superimposable upon that of the specimen obtained by the triethylamine method, showing the formation of Ic in this reaction, too. This fact seems to justify the postulation in the literature²⁾ which assumed the formation of I in the reaction 1.

The carbon tetrachloride solution of Ic was stable; 61% of it remained unchanged after 18 days. When this solution was heated under reflux in the presence of benzoic acid, a 42% decomposition in 6 hr. and a nearly complete decomposition in 14 hr. were observed. The products were benzoic anhydride and ethyl sulfite, both in yields 98% of the theoretical, and 2 mol. % of ethyl benzoate. Ether or benzene can be used as the solvent instead of carbon tetrachloride in the preparation of the mixed anhydride Ic.

n-Butyl benzoyloxysulfinate (Id) ($\text{I: R}=\text{C}_6\text{H}_5$, $\text{R}'=\text{n-C}_4\text{H}_9$) was obtained as a solution from sodium benzoate and *n*-butyl chlorosulfite by a manner similar to that which produces Ic. In its infrared spectrum (Fig. 2), strong $\text{C}=\text{O}$ and $\text{S}-\text{O}$ absorption bands appear. This anhydride gave ethyl *n*-butyl sulfite in a 54% yield when treated with anhydrous ethanol at room temperature, but no ethyl benzoate. This seems to indicate the preferable attack on sulfinyl sulfur by the anionoid reagent (reaction 5) rather than to the carbonyl group (reaction 6).

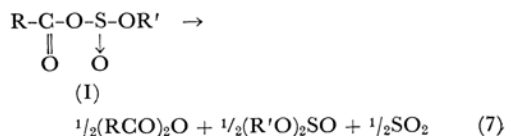


When a solution of Id in carbon tetrachloride was refluxed, a slow decomposition took place with the evolution of sulfur dioxide. This reaction was accelerated in the presence of triethylamine, re-

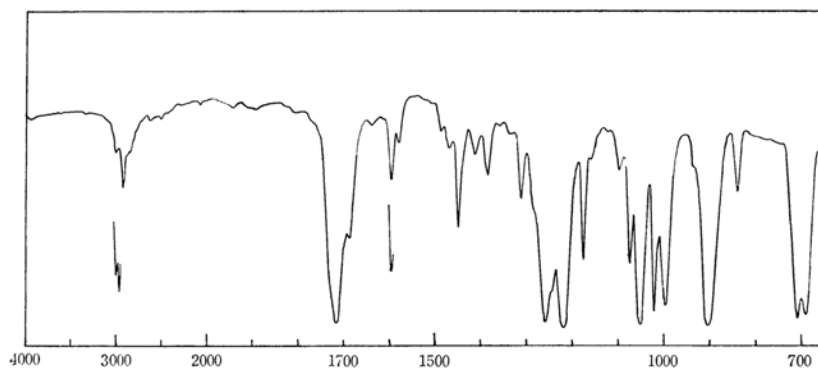
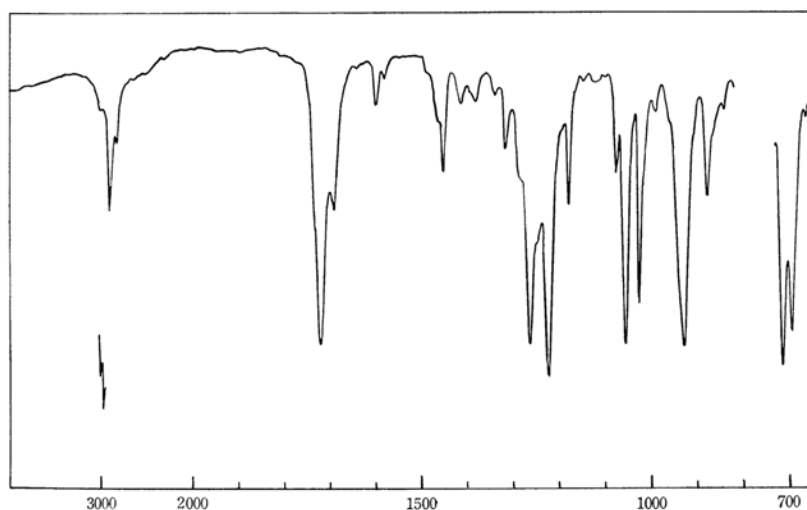
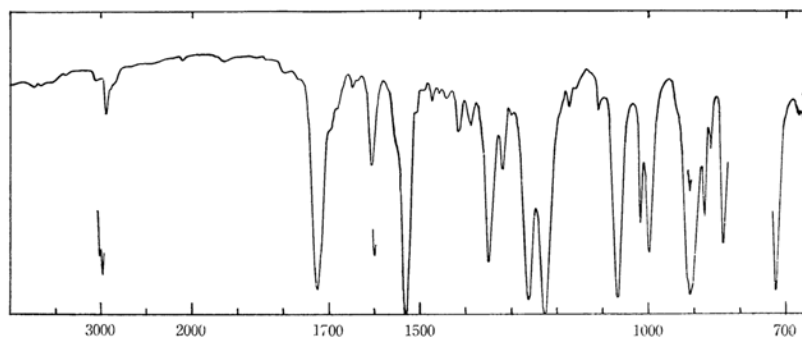
sulting in a complete decomposition within a few hours. The products were benzoic anhydride and di-*n*-butyl sulfite, both in yields 98% of the theoretical; there was only a 2% yield of *n*-butyl benzoate.

So far, no carboxylic sulfurous anhydride has been obtained in the pure crystalline state. In an attempt to get one, we attempted to prepare *p*-nitrobenzoyloxysulfinate (Ie) ($\text{I: R}=\textit{p}$ -nitrophenyl, $\text{R}'=\text{C}_2\text{H}_5$) repeatedly. The reaction of *p*-nitrobenzoic acid, ethyl chlorosulfite, and pyridine in ether, and the reaction of sodium *p*-nitrobenzoate with ethyl chlorosulfite, were examined. Both gave a solution whose infrared evidence strongly suggested the presence of the expected mixed anhydride (Fig. 3). However, the separated crystals, after the evaporation of the solvent in a vacuum at room temperature, exhibited almost the same infrared spectrum as that of *p*-nitrobenzoic acid in a KBr disk, although the melting point of the product was $85-90^\circ\text{C}$ (with decomposition), far below the 242°C of *p*-nitrobenzoic acid. Probably this compound was so sensitive to the presence of moisture that a complete hydrolysis by atmospheric moisture took place during the preparation of the KBr disk. When these crystals were shaken with carbon tetrachloride and the insoluble powder (*p*-nitrobenzoic acid) was filtered off, the infrared spectrum of the filtrate was superimposable upon Fig. 3, indicating the presence of Ic in this specimen.

Although the formation of the carboxylic ester over the postulated mixed anhydride I in a good yield has been reported in the literature,^{1,2)} most of the thermal decomposition of the carboxylic sulfurous anhydrides studied in this paper in carbon tetrachloride proceeded according to the disproportionation reaction 7, analogous to the reaction 4 observed in the carboxylic carbonic anhydride (II):



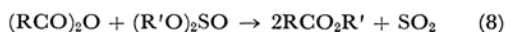
The pyrolysis of I without a solvent was also investigated. When the reaction of sodium benzoate and ethyl chlorosulfite was carried out without the solvent and when the resulting mixture was distilled under reduced pressure, the main products were again benzoic anhydride (50% of the theoretical yield) and ethyl sulfite (42% of the theoretical), while the yield of ethyl benzoate was only 5%. The pyrolysis of the reaction mixture of sodium benzoate and *n*-butyl chlorosulfite at $140-160^\circ\text{C}$ gave benzoic anhydride and di-*n*-butyl sulfite as the main products, plus *n*-butyl benzoate in a 5% yield. With a 2 molar equivalent of butyl chlorosulfite, the yield of butyl benzoate was 10%, in comparison to yield of 43% for benzoic anhydride

Fig. 1. Infrared spectrum of ethyl benzoyloxysulfinate (Ic) in CCl₄.Fig. 2. Infrared spectrum of *n*-butyl benzoyloxysulfinate in CCl₄.Fig. 3. Infrared spectrum of ethyl *p*-nitrobenzoyloxysulfinate (Ic) in CCl₄.

and 56% for di-*n*-butyl sulfite. When the reaction mixture of sodium *p*-nitrobenzoate and ethyl chlorosulfite was heated at 125°C for one hour and treated with water and ether, an insoluble powder remained in either solvent; it was identified as *p*-nitrobenzoic anhydride. The yield was 17% of the theoretical. No ethyl nitrobenzoate was detected.

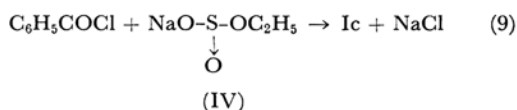
In conclusion, the thermal decomposition of the carboxylic sulfurous anhydride at a comparatively low temperature results in the disproportionation 7 as the main reaction. With elevation of the reaction temperature, the yield of the carboxylic ester shows a tendency to increase, but it is rather doubtful whether this ester is the direct result of the reaction 2. There is a good chance that this

carboxylic ester is formed by the interaction of carboxylic anhydride with dialkyl sulfite, both being the main products of the primary reaction 7. Several examples of this type of the reaction 8 have been reported⁶⁾:

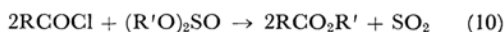


In the case of Ib in carbon tetrachloride, ethyl acetate appeared only in the later stage of the reaction, in cost of acetic anhydride, clearly indicating the occurrence of the reaction expressed by the formula 8.

Mixed anhydride I could be formed from acyl chloride and sodium monoalkyl sulfite, besides the reaction 1. For example, Ic may be prepared by the interaction of benzoyl chloride and sodium ethyl sulfite (IV), as shown below:



When IV, prepared from sodium ethylate and sulfur dioxide, was treated with benzoyl chloride without the solvent, the reaction proceeded very slowly at room temperature. At a higher temperature, benzoic anhydride in a 53% yield, ethyl sulfite in a 50% yield and ethyl benzoate in a 10% yield were obtained, suggesting the expected formation of the intermediate Ic according to the reaction 9. When both reactants were left in carbon tetrachloride at room temperature for 3 days, 80% of the starting materials remained unchanged. Benzoic anhydride was formed in an amount 20% of the theoretical yield, while no indication of Ic itself was observed, even in the infrared spectrum. Only a slight amount of ethyl benzoate was there at first, but about 12 mol. % of it was detected when the filtrate from the unchanged IV was kept at room temperature for one week. Most probably it arises from the interaction of benzoyl chloride and ethyl sulfite, one of the primary products. This type of the reaction, 10, has also been known to occur with some acyl chlorides⁶⁾:



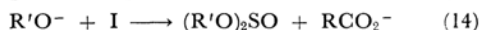
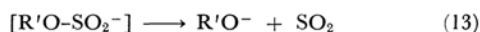
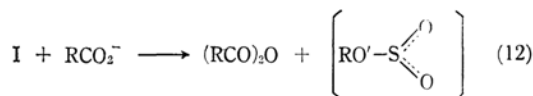
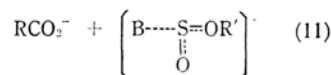
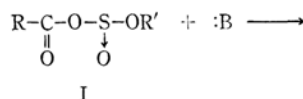
The failure to detect the intermediate Ic may be attributable to the slowness of the reaction 9, during which the disproportionation 7 of the once-formed Ic proceeds (probably by a catalytic acceleration of IV itself as a base).

The disproportionation (7) may be concluded to be a base catalytic from the effect of triethylamine to accelerate the decomposition of Id, as has been described above, and also on the basis of the following evidence. Ethyl chlorosulfite was added to a solution of benzoic acid in pyridine, and the reaction mixture was warmed at 70°C for half an hour, diluted with water, and extracted with

ether to give benzoic anhydride in a 55% yield, ethyl sulfite in a 27% yield, and a trace of ethyl benzoate. This experiment showed that Ic was decomposed even under these mild conditions, while refluxing for more than 10 hr. was necessary to complete the decomposition of Ic in carbon tetrachloride in the absence of a base. The above experiment also suggests that the rate of the reaction between the carboxylate anion and alkyl chlorosulfite is very fast, since the chlorosulfites are known to be decomposed by pyridine to form alkyl chlorides and sulfur dioxide with great ease.⁷⁾

On the other hand, the decomposition of Ic in the presence of benzoic acid in carbon tetrachloride caused the disproportionation 7, although at a much slower rate than the base-catalytic one.

The following mechanism may be proposed for the disproportionation 7, where B means base catalyst:

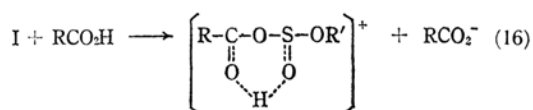


The anionoid attack on I occurred on the sulfinyl sulfur preferentially, not on carbonyl, as shown in the reaction of Id with ethanol. The attraction of an anionoid reagent to the positive center on sulfur atom, the linkage of which to the sulfinyl oxygen bears a strong semipolar character,⁸⁾ may be the reason for this difference in reactivity. The attack by the carboxylate anion on I also could take place on the sulfur atom, but it would form another I (15), with the net result of no apparent reaction:



Therefore, the only fruitful attack is the one expressed in 12, giving acyl anhydride.

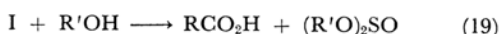
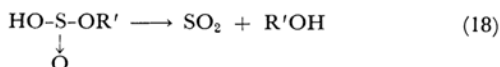
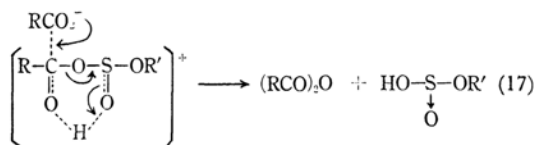
Decomposition in the presence of the carboxylic acid was considered to proceed as is shown below:



7) J. Kenyon, H. Phillips and F. M. H. Taylor, *J. Chem. Soc.*, **1931**, 382; C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953).

8) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., N. Y. (1962).

6) R. Levaillant, *Compt. rend.*, **190**, 55 (1930).



Infrared Spectra of the Carboxylic Sulfurous Anhydride.—The wave numbers of the C=O and S—O stretching bands of several derivatives of I are shown in Table I.

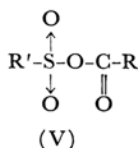
TABLE I

R	R'	Peak position ^{a)}	
		C=O, cm ⁻¹	S—O, cm ⁻¹
Methyl	Methyl	1757	1196
Methyl	Ethyl	1752	1190
Phenyl	Ethyl	1724	1222
Phenyl	<i>n</i> -Butyl	1723	1223
Phenyl	Phenyl ^{b)}	1729	1230
<i>p</i> -Nitrophenyl	Ethyl	1730	1227

a) In CCl₄.

b) In ether. This compound will be described in detail later.

The wave numbers of the C=O absorptions of these compounds are close to those of the carboxylic carbonic anhydrides (for example, 1755 cm⁻¹ for II: R=methyl, R'=ethyl; 1739 cm⁻¹ for II: R=phenyl, R'=ethyl,⁹⁾ and they lie in a lower frequency region than that of the carboxylic sulfonic anhydride V¹⁰⁾ (1780 cm⁻¹ for V: R=phenyl, R'=phenyl; 1800 cm⁻¹ for V: R=ethyl, R'=phenyl).



Experimental

1. Methyl Acetoxysulfinate (Ia).—When, to 4.5 g. of a fine powder of sodium acetate (VI) which had been dehydrated at 200°C in vacuum for a few hours, there was added 6.5 g. of methyl chlorosulfite drop by drop, with constant shaking and good cooling, the reaction started at once, and heat was evolved. After 5 hr. at room temperature, the jelly-like reaction mixture was distilled in vacuo to give 4.5 g. of a colorless, mobile liquid at 37–39°C/1 mmHg in a 60% yield of the theoretical; infrared spectrum, 1752 (C=O), 1210 (S—O), 940, and 690 cm⁻¹ (neat). This compound reacted with water very rapidly. In a small vial with a ground

glass stopper there was weighed 365.0 mg. of this ample, which had been stored for 2 weeks in a refrigerator; the sample was then hydrolyzed with a solution of 2 g. of sodium hydroxide in 20 ml. of water in a closed vessel. The oil dissolved in less than one minute, thus forming a clear solution, which was then oxidized with 6 ml. of 30% hydrogen peroxide for 2 hr. Diluted hydrochloric acid was added to this solution, and the sulfate anion was precipitated as barium sulfate (551.9 mg.).

S: Found: 20.8%. Calcd. for C₃H₆O₄S: 23.3%.

2. Ethyl Acetoxysulfinate (Ib).—**2.1. Reaction without a Solvent.**—From 12.5 g. of ethyl chlorosulfite (VII) and 8.0 g. of VI, 8.3 g. of Ib was obtained as a colorless liquid (b. p. 44°C/1 mmHg) by a manner similar to that used for Ia. The yield was 56% of the theoretical. This sample (169.7 mg.) gave 249.5 mg. of barium sulfate.

S: Found: 20.2%. Calcd. for C₄H₈O₄S: 21.1%.

2.2. Reaction in Carbon Tetrachloride.—A solution of 3.0 g. of VII in 50 ml. of carbon tetrachloride was added to 2.2 g. of VI, shaken well for 30 min., and filtered through a fritted glass funnel. The infrared spectrum of the filtrate was almost entirely superimposable upon that of the specimen obtained in 2.1. IR: 1752, 1190, 1000, 898, 700 cm⁻¹. After one day, no change was observed in the infrared spectrum.

2.3. The Decomposition of Ib.—A carbon tetrachloride solution of Ib (4.7 × 10⁻¹ mol./l.) was refluxed to produce acetic anhydride in a 40% yield in 3 hrs, and in a 55.5% yield in 6 hr. When it was boiled for another 6 hr., the concentration of acetic anhydride was decreased to 11% and replaced by ethyl acetate in a 27.5% yield. (The determinations were made by the infrared spectroscopic method.)

3. Ethyl Benzoyloxysulfinate (Ic).—**3.1. Preparation.**—Benzoic acid (6.9 g.) and VII (7.3 g.) were dissolved in 180 ml. of carbon tetrachloride; no change was observed. When 6.8 g. of triethylamine was added drop by drop to this solution cooled in an ice bath, a vigorous reaction occurred, with the precipitation of white crystals; these crystals were identified as triethylamine hydrochloride. The infrared spectrum of the filtrate is shown in Fig. 1. When this filtrate was evaporated under reduced pressure at room temperature, with precaution taken to avoid moisture, it gave a pale sirup which solidified to a glassy mass at -70°C. When it came in contact with moisture, this sirup formed crystals of benzoic acid rapidly. After a carbon tetrachloride solution of Ic (3.14 × 10⁻¹ mol./l. as 100% pure) had been refluxed for 6 hr., an aliquot of it was washed with a diluted potassium carbonate solution and water successively, and then dried over magnesium sulfate. By its infrared spectrum the presence of 5.73 × 10⁻² mol./l. of benzoic anhydride and 5.72 × 10⁻² mol./l. of ethyl sulfite was detected. At this stage of the reaction, the yield of two products was 34% of the theoretical and in an equimolecular ratio. The main portion of the solution of Ic was refluxed for another few hours and finally evaporated to expel the solvent, after which the residue was heated in an oil bath for one hour to complete the decomposition. After it had been diluted with carbon tetrachloride, this residue was analyzed by infrared spectroscopy and so found to contain benzoic anhydride and ethyl sulfite in a 1.15:1.00 molar ratio. A few grams of aniline were added to this solution to remove benzoic anhydride as almost insoluble

9) D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958); 4b.

10) C. Overberger and E. Sarlo, *J. Am. Chem. Soc.*, **85**, 2446 (1963).

benzanilide (identified by melting point and infrared spectrum); The filtrate was then washed repeatedly with a potassium carbonate solution and dried over magnesium sulfate. The infrared spectrum of this solution revealed the presence of a small amount of ethyl benzoate, which was masked by benzoic anhydride before the treatment with aniline. The yields of benzoic anhydride, ethyl sulfite and ethyl benzoate were 94%, 82%, and 6% of the theoretical yield respectively.

3.2. The Decomposition of Ic in the Presence of Acid. When a solution of Ic (1.90×10^{-1} mol./l.) and benzoic acid (8.45×10^{-2} mol./l.) in carbon tetrachloride was refluxed, the yield of benzoic anhydride was 42% of the theoretical in 3 hr, and 98% in 14 hr. The corresponding yield of ethyl sulfite was also 98% in 14 hr. By treatment with aniline as described in 3.1, the yield of ethyl benzoate was estimated to be 2.4%. Therefore, 98% of the decomposition of Ic in this condition was shown to proceed according to the reaction 7, leaving only 2% at most for the reaction 2. The slightly higher yield of ethyl benzoate in 3.1 may be attributable to the high reaction temperature in the last stage of the reaction without the solvent, during which stage some of benzoic anhydride may react with ethyl sulfite to give ethyl benzoate following the reaction 8.

3.3. Formation from Sodium Benzoate.—Two grams of sodium benzoate and 1.7 g. of VII were mixed and extracted with 100 ml. of carbon tetrachloride after the initial exothermic reaction was over. The infrared spectrum of this extract was almost identical with that shown in Fig. 1, indicating the formation of the same mixed anhydride Ic. After 18 days, this solution was found by infrared analysis still to contain 61% of original Ic.

3.4. Decomposition without a Solvent.—Nine grams of VII was added to 10.0 g. of sodium benzoate, and the resultant gel-like mixture was distilled under reduced pressure. The redistillation of the total distillate gave the forerun, consisting of 2.0 g. of ethyl sulfite (42% of the theoretical yield), 0.5 g. of ethyl benzoate (4.8 mol.%), and 4.0 g. of benzoic anhydride (51% of the theoretical yield), b. p. $170-171^{\circ}\text{C}/5$ mmHg.

3.5. Reaction with Ethanol.—To a reaction mixture of 5.5 g. of sodium benzoate and 5.0 g. of VII 5 ml of ethanol (absolute) was added, after the initial vigorous reaction had subsided. The work-up of this mixture gave 2.0 g. of ethyl sulfite (38%), with no ethyl benzoate. The amount of benzoic acid recovered was 4.0 g. (82%). Therefore, ethanol attacked Ic on the sulfur atom, not on carbonyl.

3.6. The Reaction in Pyridine.—Benzoic acid (6.5 g.) was dissolved in 20 ml. of dry pyridine and cooled in an ice bath. When 7.0 g. of VII was added to this solution, no gas evolved and no precipitate appeared. After it had been heated in an oil bath for 30 min. at 70°C , the solution was diluted with a lot of water, made acidic with hydrochloric acid, and extracted with ether. The usual work-up gave 0.7 mol. % of ethyl benzoate, ethyl sulfite in 27.2% of the theoretical yield, and benzoic anhydride in a yield 55% of the theoretical.

4. *n*-Butyl Benzoyloxysulfinate.—**4.1. Preparation in Carbon Tetrachloride.**—When 2.5 g. of triethylamine was added to a solution of 2.8 g. of benzoic acid and 3.5 g. of *n*-butyl chlorosulfite (VIII) (b. p. $70^{\circ}\text{C}/13$ mmHg) in 62 ml. of carbon tetrachloride, triethylamine hydrochloride was precipitated at once. The

infrared spectrum of the filtrate is shown in Fig. 2; it has a close similarity to that of the ethyl analog. (i) Anhydrous ethanol (5 ml.) was added to 10 ml. of this solution, and the mixture was warmed, washed with water and aqueous sodium hydrogen carbonate successively, and dried over magnesium sulfate. The infrared spectrum of the filtrate coincided with that of ethyl *n*-butyl sulfite. The yield was estimated by infrared analysis to be 54% of the theoretical. No ethyl benzoate was detected. (ii) Triethylamine (0.5 g.) was added to the remaining solution of the mixed anhydride Id; this mixture was then refluxed for a few hours, during which the evolution of sulfur dioxide was completed. The formation of benzoic anhydride and di-*n*-butyl sulfite, each in a 98% yield of the theoretical, was confirmed by the infrared spectroscopy. After treatment with aniline, *n*-butyl benzoate in a 2.1% yield was detected.

4.2. Reaction without a Solvent.—(i) A reaction mixture of 7.5 g. of sodium benzoate and 10.0 g. of VIII (equimolecular) was heated at $140-160^{\circ}\text{C}$ for 2 hr. and diluted with water. The deposited oil was washed with aqueous sodium hydrogen carbonate, dried over magnesium sulfate, and distilled under reduced pressure to give a forerun consisting of 1.5 g. (31% of the theoretical yield) of di-*n*-butyl sulfite and 0.5 g. of butyl benzoate (5%) at $119-126^{\circ}\text{C}/26$ mmHg and 1.5 g. of benzoic anhydride (26% of the theoretical yield) at $207^{\circ}\text{C}/25$ mmHg. (ii) The reaction of 6.0 g. of sodium benzoate and 12 g. (1.9 mol.) of VIII was carried out as above. After they had been heated at $140-180^{\circ}\text{C}$ for one and a half hours, the products were extracted with ether. Vacuum distillation gave 2.2 g. of di-*n*-butyl sulfite (56% of the theoretical yield), 0.7 g. of butyl benzoate (10 mol.%) and 2.0 g. of benzoic anhydride (43% of the theoretical yield).

5. Ethyl *p*-Nitrobenzoyloxysulfinate (Ie).—**5.1. Formation in Carbon Tetrachloride.**—VII (3 g.) was added to a suspension of 4.5 g. of sodium *p*-nitrobenzoate, which had been finely ground and dehydrated in a vacuum at 140°C for 3 hr., in 50 ml. of carbon tetrachloride. The reaction mixture was shaken occasionally and filtered, after 1.5 hrs., through a fritted glass funnel. The infrared spectrum of the filtrate (Fig. 3) exhibited strong C=O and S=O absorptions. With caution taken to avoid moisture, this filtrate was concentrated under reduced pressure; this left almost colorless crystals (m. p. $85-90^{\circ}\text{C}$) (with decomposition). Its infrared spectrum in a KBr disk was almost the same as that of *p*-nitrobenzoic acid. When 2.7 g. of this specimen was shaken with 20 ml. of carbon tetrachloride, 2 g. remained undissolved, and the filtrate showed an infrared spectrum identical with that in Fig. 3, indicating the presence of Ie in the above specimen, probably contaminated with nitrobenzoic acid.

5.2. Formation in Toluene.—Sodium *p*-nitrobenzoate (10.0 g.) was suspended in 40 ml. of toluene, which had been dehydrated by boiling it over molten sodium, and treated with 8.5 g. of VII. The gel-like white precipitate was filtered off, and the filtrate was cooled in a dry ice-ethanol bath at -66°C to deposit pale crystals. About 50 ml. of petroleum ether was then added to decrease the solubility, and the supernatant was removed by decantation, thus leaving 5 g. of crystals (m. p. $85-90^{\circ}\text{C}$). Its infrared spectrum in

a KBr disk again coincided with that of *p*-nitrobenzoic acid.

5.3. *Decomposition without a Solvent.*—A reaction mixture of 7.3 g. of sodium *p*-nitrobenzoate and 10.5 g. of VII (2.1 molar equivalent) was heated in an oil bath at 125°C for one hour. Ether and water were added to the mass after it had been cooled. One gram of the white powder, identified as *p*-nitrobenzoic anhydride, remained undissolved. The yield was 17% of the theoretical yield. A lot of nitrobenzoic acid was recovered, but no ethyl *p*-nitrobenzoate was detected. The low yield of the acid anhydride may be attributed to the too mild reaction conditions, insufficient to bring about the complete decomposition of the mixed anhydride Ie.

6. Reaction between Benzoyl Chloride and Sodium Ethyl Sulfite.—6.1. *Without a Solvent.*—Sodium ethyl sulfite (IV) was prepared by passing dry sulfur dioxide into sodium ethoxide in ethanol and by evaporating the mixture to dryness under reduced pressure; it was finally dried in a vacuum for 3 hr. To 6.5 g. of this salt there was then added 7.0 g. of benzoyl chloride. After one hour at room temperature, the mixture was subjected to vacuum distillation to recover most of the starting materials unchanged. When the same amounts of the reactants were, in another experiment, heated at 120°C for few hours, 500 ml. of sulfur dioxide (about 40 mol.%) evolved. The vacuum distillation of the remaining mass gave

3.0 g. of the forerun at 50–70°C/80 mmHg and 3.0 g. of benzoic anhydride (52% of the theoretical yield), m. p. 41°C. The forerun was found by the infrared analysis to contain 1.75 g. of ethyl sulfite (50% of the theoretical) and 0.75 g. of ethyl benzoate (10 mol.%).

6.2. *Reaction in Carbon Tetrachloride.*—To a suspension of 1.5 g. of IV 1.5 g. of benzoyl chloride was added; the mixture was kept in a desiccator and occasionally shaken over a 4-day period, and then filtered from the insoluble powder. The infrared spectrum of the filtrate showed that 10.1 mol.% (20.2% of the theoretical yield) of benzoic anhydride was produced, although a large part of the benzoyl chloride remained unaltered. The key bands of ethyl benzoate were weak in this filtrate at first, and those of ethyl sulfite were masked by benzoyl chloride. After 6 days, benzoyl chloride and benzoic anhydride were decomposed by aniline to benzanilide and filtered off. The filtrate was washed by diluted hydrochloric acid, aqueous potassium carbonate and water successively, and found by the infrared spectroscopy to contain 12.2 mol.% of ethyl benzoate and 4.3 mol.% of ethyl sulfite. If the same molar (10.1 mol.%) of ethyl sulfite as benzoic anhydride was assumed to have existed in the first filtrate, the difference (5.8 mol.%) may be considered to have converted into 11.6 mol.% of ethyl benzoate, in accordance with the observed value, probably by the reaction 9.