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Mechanism of Decomposition of Carboxylic Sulfurous Anhydrides[*1]

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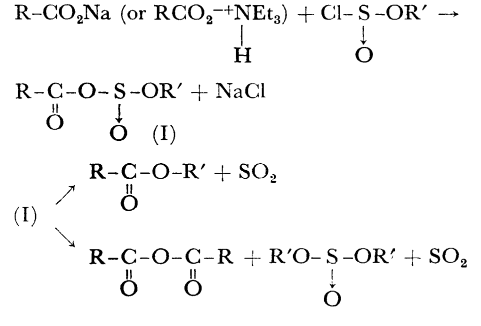
Ethyl benzoyloxysulfinate, prepared from ^{18}O-labeled benzoic acid and ethyl chlorosulfite, was decomposed and the products were analyzed. The ^{18}O analyses showed that; 1) prior to decomposition the ^{18}O of the mixed anhydride was scrambled due to the formation and the internal return of an ion-pair, $C_6H_5\underset{O}{\underset{\|}{C}}{}^{+}\,{}^{-}O\underset{O}{\underset{\|}{S}}OEt$; 2) ethyl benzoate, benzoic anhydride and diethyl sulfite were produced *via* an ionic chain mechanism involving successive attack of ethoxide anion and benzoate anion on the carbonyl carbon and sulfinyl sulfur of the mixed anhydride.

In the thermal decomposition of mixed anhydride (I), formed from a carboxylic acid and an alkyl hydrogen sulfite, products are sulfur dioxide, a carboxylic ester, a carboxylic anhydride, and dialkyl sulfite, as shown in Eqs. (1) and (2).[1] In a previous paper[2] we described the isolation and the infrared spectra of I with various R and R′, and discussed the mechanism of the formation of a carboxylic ester by use of ^{18}O-labled methyl and phenyl benzoyloxysulfinates.

In order to clarify the mechanism of the formation of all the decomposition products, the ^{18}O contents of all the products from the decomposition



$$R\text{-}CO_2Na\ (\text{or } RCO_2^{-}\,{}^{+}\underset{H}{\underset{|}{N}}Et_3) + Cl\text{-}\underset{O}{\underset{\downarrow}{S}}\text{-}OR' \rightarrow$$

$$R\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}\underset{O\ (I)}{\underset{\downarrow}{S}}\text{-}OR' + NaCl \qquad (1)$$

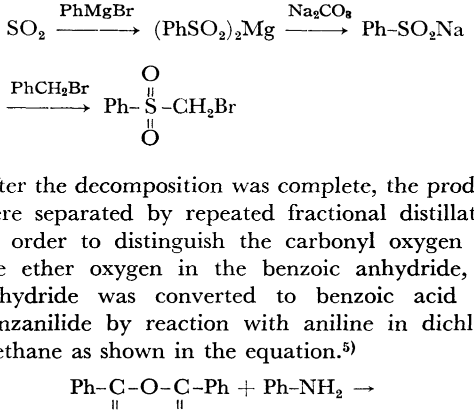
$$(I) \nearrow R\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}R' + SO_2 \qquad (2)$$

$$(I) \searrow R\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}\underset{O}{\underset{\|}{C}}\text{-}R + R'O\text{-}\underset{O}{\underset{\downarrow}{S}}\text{-}OR' + SO_2 \qquad (3)$$

of ^{18}O-labeled ethyl benzoyloxysulfinate (Ia, R= -Ph, R′=-C_2H_5) have been analyzed in detail, and the results are presented in this paper.

Results and Discussion

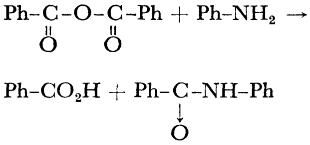
When ^{18}O-labeled sodium benzoate and ethyl chlorosulfite were mixed and the sirupy mixture formed was heated at 110—120°C, it decomposed with vigorous evolution of sulfur dioxide. The sulfur dioxide was collected in a dry ice-acetone trap, and was converted to benzyl phenyl sulfone for the ^{18}O analysis according to the equation.



$$SO_2 \xrightarrow{PhMgBr} (PhSO_2)_2Mg \xrightarrow{Na_2CO_3} Ph\text{-}SO_2Na$$

$$\xrightarrow{PhCH_2Br} Ph\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}CH_2Br \qquad (4)$$

After the decomposition was complete, the products were separated by repeated fractional distillation. In order to distinguish the carbonyl oxygen and the ether oxygen in the benzoic anhydride, the anhydride was converted to benzoic acid and benzanilide by reaction with aniline in dichloromethane as shown in the equation.[5]



$$Ph\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}\underset{O}{\underset{\|}{C}}\text{-}Ph + Ph\text{-}NH_2 \rightarrow$$

$$Ph\text{-}CO_2H + Ph\text{-}\underset{O}{\underset{\downarrow}{C}}\text{-}NH\text{-}Ph \qquad (5)$$

TABLE 1. SPECIFICITY OF ^{18}O-LABELING

Sample	% ^{18}O-excess	% ^{18}O-calcd	
Starting $PhCO_2Na$	1.30	(1.30)	1
$PhCOOC_2H_5$*	0.67	0.65	1/2
$(EtO)_2SO$*	0.31	0.22	1/6
$PhSO_2CH_2Ph$ (←SO_2*)	0.60	0.65	1/2
$Ph\underset{O}{\underset{\|}{C}}O\underset{O}{\underset{\|}{C}}Ph$*	1.00	1.08	5/6
$PhCO_2H$**	1.00	1.07	13/16
PhCONHPh**	1.00	1.14	7/8

* Direct reaction products.
** Derived from benzoic anhydride.

[*1] Organic Sulfur Compound. XX.

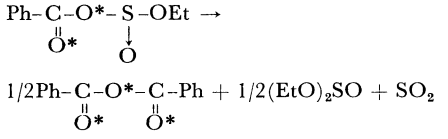
[1] M. Kobayashi and A. Yamamoto, This Bulletin, **39**, 961 (1966).

[2] M. Kobayashi and R. Kiritani, *ibid.*, **39**, 1782 (1966).

[3] D. B. Denney and M. A. Greenbaum, *J. Amer. Chem. Soc.*, **79**, 3701 (1957).

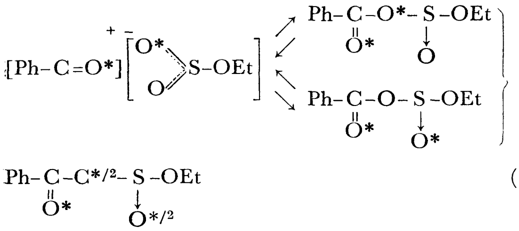
The results of ^{18}O analyses of all the reaction products are shown in Table 1.

The ^{18}O-atom % of ethyl benzoate was one half of that of the starting sodium benzoate. This finding indicates that, as shown previously, the ester was formed not by the reaction between ethyl chlorosulfite and benzoic anhydride, but formed directly by the decomposition of the mixed anhydride Ia. It should be noted that diethyl sulfite contained an appreciable amount of ^{18}O, and the ^{18}O content observed for benzoic anhydride was smaller than the value calculated on the basis of the reaction



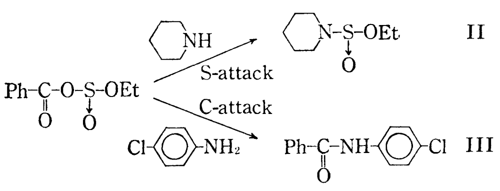
$$\mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}{-}O^*{-}\underset{O}{\underset{\downarrow}{S}}{-}OEt} \rightarrow$$
$$\mathrm{1/2Ph{-}\underset{O^*}{\underset{\|}{C}}{-}O^*{-}\underset{O^*}{\underset{\|}{C}}{-}Ph + 1/2(EtO)_2SO + SO_2} \qquad (6)$$

The unexpected data can be explained by the assumption that Ia dissociates reversibly to form an ion pair of benzoyl cation and ethoxysulfinate anion according to Eq. (7). When the scrambling of ^{18}O due to internal return of the ion pair is taken into consideration, the ^{18}O contents and distribution in other products are also explained.



$$\overset{+}{[}\mathrm{Ph{-}C{=}O^*}]\overset{-}{\left[\begin{matrix}\mathrm{O^*}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{S{-}OEt}\right]} \rightleftarrows \left\{\begin{matrix}\mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}{-}O^*{-}\underset{O}{\underset{\downarrow}{S}}{-}OEt}\\ \mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}{-}O{-}\underset{O^*}{\underset{\downarrow}{S}}{-}OEt}\end{matrix}\right\}$$
$$\mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}{-}C^{*/2}{-}\underset{O^{*/2}}{\underset{\downarrow}{S}}{-}OEt} \qquad (7)$$

Reaction between Ia and Bases. Piperidine and *p*-chloroaniline were used as examples of a strong base and a weak base respectively. The only product isolated from the reaction between piperidine and Ia was the S-attack product, II,[4] whereas the only product isolated from the reaction between *p*-chloroaniline and Ia was the C-attack product, III, as shown in the following equation.



(8)

Since each of two derivatives contains a carbonyl oxygen and a sulfinyl oxygen, respectively, it is possible to determine the ^{18}O-distribution in Ia by the analyses of these two derivatives. The ^{18}O atom % found for II and III are shown in Table 2.

The ^{18}O content of the S-attack product, II, increased with time between the formation of Ia and the addition of piperidine, whereas that of the C-attack product, III, remained constant and was equal to that of the original benzoic acid. These findings indicate that it takes a little while for the oxygens to be scrambled completely through formation and internal return of ion-pairs at room temperature.

Table 2. Specificity of ^{18}O-labeling

Sample	% ^{18}O-excess
Starting PhCOOH	1.32
II (12 hr after formation of Ia)*	0.19
II (36 hr after formation of Ia)*	0.22
III	1.32

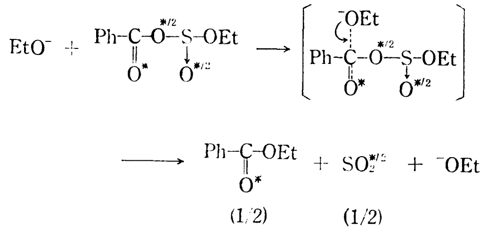
* at room temperature

Both the reaction between Ia and aniline and that between Ia and hydrazine yielded unidentifiable brown tar, which was probably produced from the decomposition of the S-attack products, $\mathrm{Ph{-}NH{-}\underset{O}{\underset{\downarrow}{S}}{-}OEt}$ and $\mathrm{H_2NNH{-}\underset{O}{\underset{\downarrow}{S}}{-}OEt}$. Neither *p*-nitroaniline nor 2,5-dichloroaniline reacted with Ia when they were mixed with Ia and the mixture was allowed to stand at room temperature for several hours.

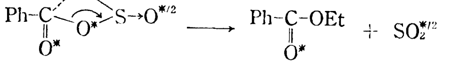
Isolation of Ia. Ia was unstable to water and was hydrolyzed rapidly. However, it was thermally stable, and it was possible to obtain white crystals of Ia by distillation in a high vacuum.

Reaction Mechanisms. The observed ^{18}O contents of all the reaction products are best explained by the reaction steps involving formation and internal return of the ion-pair and the successive attack of both benzoate anion and ethoxide anion to Ia by an ionic chain mechanism.

The most plausible route for formation of ethyl benzoate is direct attack of ethoxide anion to the carbonyl carbon of Ia, Eq. (9), or to that of the ion pair, Eq. (7). However, an S$_N$*i*-type mechanism, as shown in Eq. (10) cannot be ruled out by the results of the ^{18}O analyses alone. The fractions shown in the parentheses under the ^{18}O-containing compounds indicate the ratio of the excess ^{18}O content calculated for the compound versus the excess ^{18}O content of the starting benzoic acid.



$$\mathrm{EtO^-} + \mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}{-}O^{*/2}{-}\underset{O^{*/2}}{\underset{\downarrow}{S}}{-}OEt} \longrightarrow \left[\mathrm{Ph{-}\underset{O^*}{\underset{\|}{\overset{{}^-OEt}{C}}}{-}O^{*/2}{-}\underset{O^{*/2}}{\underset{\downarrow}{S}}{-}OEt}\right]$$
$$\longrightarrow \underset{(1/2)}{\mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}{-}OEt}} + \underset{(1/2)}{\mathrm{SO_2^{*/2}}} + \mathrm{{}^-OEt} \qquad (9)$$



$$\mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}\overset{OEt}{\frown}O^*{>}S{\rightarrow}O^{*/2}} \longrightarrow \mathrm{Ph{-}\underset{O^*}{\underset{\|}{C}}{-}OEt} + \mathrm{SO_2^{*/2}} \qquad (10)$$

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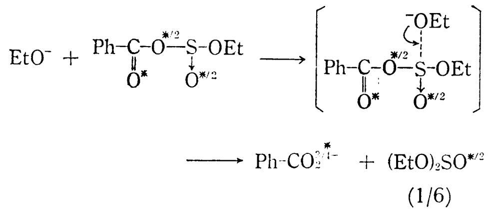
4) G. Zinner, *Chem. Ber.*, **91**, 969 (1958).

The attack of the ethoxide anion on the sulfinyl sulfur atom of Ia will yield ethyl sulfite and benzoate anion, and the attack of the benzoate anion thus formed on the carbonyl carbon of Ia will yield benzoic anhydride, according to Eqs. (11) and (12). The analyses of the ^{18}O content of the products should determine whether or not Eq. (11) or (12) represent the reaction taking place in this medium. The benzoic anhydride was converted to benzanilide and benzoic acid according to Eq. (13). The result of the ^{18}O analyses of benzoic anhydride, benzoic acid, ethyl sulfite and sulfur dioxide (see Table 1) shows that Eqs. (11) and (12) actually represent the reaction taking place in this medium.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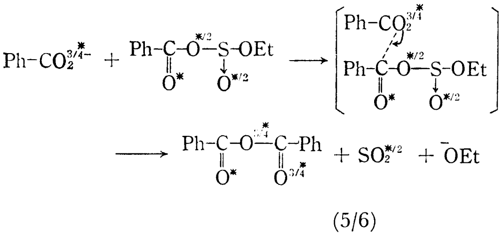
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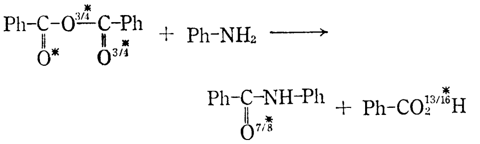
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Experimental

^{18}O-Labeled Benzoic Acid. According to a previous method[2] a mixture of 25 g of benzotrichloride and of $H_2{}^{18}O$ (1.30 excess-^{18}O atm %) was refluxed and shaken for 20 hr in a bath at 110°C. After the hydrogen shaken for 20 hr in a bath at 110°C. After the hydrogen chloride formed and excess water were removed under reduced pressure, and the crystals of the benzoic acid remaining were converted to sodium benzoate by addition of the equimolar amount of a sodium hydroxide solution. The sodium salt was recrystallized from distilled water, ground to fine powder, and then dried in a vacuum at 100°C for 2 hr. Yield 14.2 g.

Ethyl Chlorosulfite. To 100 g of thionyl chloride 35.8 g of methanol was slowly added while the temperature was kept low with ice-cooling. The mixture was allowed to stand at room temperature for three days. Distillation under reduced pressure gave 61.5 g of ethyl chlorosulfite (bp 34.5°C/23 mmHg). Yield 61.5%.

Thermal Decomposition of Ethyl Benzoyloxysulfinate (Ia). When 17.85 g of ethyl chlorosulfite was added to 10 g of well-dried sodium benzoate-^{18}O, a slightly exothermic reaction occurred. The milky reaction mixture was then heated at 110—130°C for 2 hr. The sulfur dioxide which evolved vigorously during this period was dried with calcium chloride and introduced into an ethereal solution of phenylmagnesium bromide.[5] The yield of sodium benzenesulfinate was 6.63 g. After the salt was recrystallized from absolute methanol and dried, it was converted to phenyl benzyl sulfone by heating it with benzyl bromide in a sealed tube at 110°C for 5 hr.

The residual reaction mixture was refluxed at 190°C for 2 hr to complete the decomposition. The cooled reaction mixture was treated with 40 m*l* of methylene chloride, and the sodium chloride precipitated was filtered off. After the solvent was removed in a vacuum, repeated fractional distillation of the residue under reduced pressure yielded 2.1 g of diethyl sulfite (bp 68°C/30 mmHg), 0.7 g of ethyl benzoate (bp 105—108°C/30 mmHg), and 2.1 g of benzoic anhydride (bp 190—200°C/30 mmHg).

The benzoic anhydride obtained above was converted to benzanilide and benzoic acid by allowing a mixture of 1.0 g of benzoic anhydride and 0.5 g of aniline to stand at room temperature for a few minutes. White crystals of benzanilide which precipitated were filtered off and recrystallized from ethanol; yield, 500 mg. The filtrate was shaken well with a sodium carbonate solution, and the aqueous layer yielded, upon acidification with a diluted hydrochloric acid, crystals of benzoic acid, which were recrystallized from *n*-hexane; yield, 300 mg.

Reaction between Ia and Piperidine. To 500 m*l* of a carbon tetrachloride solution containing 2 g of benzoic acid and 2.1 g of ethyl chlorosulfite was added 2 g of triethylamine drop by drop with ice-cooling. When 1.7 g of piperidine was added to this mixture, the solution turned pale yellow. After it was allowed to stand overnight at room temperature, 50 m*l* of water was added to remove triethylamine hydrochloride. The organic layer separated was dried over magnesium sulfate. After the solution was removed in a vacuum, the residual yellow-brown liquid was distilled under reduced pressure and 0.5 g of an oil boling at 90°C/5 mmHg was obtained, which was found to be II by comparison of its infrared spectrum with that of the authentic sample prepared from ethyl chlorosulfate and piperidine.

Reaction between Ia and *p*-Chloaniline. To 30 m*l* of benzene solution containing 2 g of benzoic acid and 2.1 g of ethyl chlorosulfite was added 2 g of triethylamine with ice-cooling. The triethylamine hydrochloride precipitated was filtered off, and 30 m*l* of a carbon tetrachloride solution containing 2 g of *p*-chloroaniline was added to the filtrate. After the mixture was allowed to stand at room temperature for one hour, white crystals of *p*-chlorobenzanilide precipitated; yield, 130 mg.

Isolation of Ia. When 5 g of well-dried sodium benzoate and 10 g of ethyl chlorosulfite were mixed, an exothermic reaction takes place and the mixture became sirupy. Distillation in a high vaccum yielded a crystalline distillate at 94 °C/4×10^{-3} mmHg, which was found to be Ia on the basis of its infrared spectrum and the finding that upon addition of an ethereal solution of

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[5] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, 226 (1956).

p-chloroaniline it yielded crystalline *p*-chlorobenzanilide.

^{18}O-Analyses. The ^{18}O analyses were carried out according to the method of Rittenberg and Ponticorvo.[6)] Each sample was pyrolyzed in the presence of mercuric chloride and mercuric cyanide at 400°C for 4 hr, and the ^{18}O atom % of the carbon dioxide produced was determined by use of a Hitachi RMU-6D type mass spectrometer.

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6) D. Rittenberg and L. Ponticorvo, *Int. J. Appl. Rad. Isotopes.*, **1**, 208 (1956).