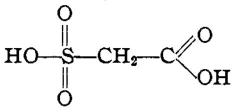
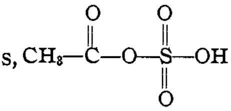
[COMMUNICATION NO. 682 FROM THE KODAK RESEARCH LABORATORIES]

The Rates of Formation of Sulfoaliphatic Acids*

BY T. F. MURRAY, JR., AND W. O. KENYON

Anhydrides of aliphatic acids are in common use as acylating agents, often in conjunction with sulfuric acid as the catalyst. Little attention apparently has been given to the fate of sulfuric acid when employed as an acylation catalyst, though Franchimont[1] as early as 1881 showed that sulfoacetic acid,  $HO{-}S(=O)_2{-}CH_2{-}C(=O)OH$, forms when acetic anhydride and sulfuric acid react. He suggested that the reaction mechanism involved the primary formation of a mixed anhydride of sulfuric and acetic acids,  $CH_3{-}C(=O){-}O{-}S(=O)_2{-}OH$ (sometimes called acetyl sulfuric acid), which subsequently rearranges to the sulfo-acid. Anhydrides of aliphatic acids of three or more carbon atoms produce α-sulfo-acids by this method,[1] which have been resolved into their optical isomers.[2]

alpha-Sulfoaliphatic acids have been produced by other methods including the action of sulfur trioxide[3] or chlorosulfonic acid[4] on aliphatic acids, the oxidation of isethionic acid with chromic acid,[5] the action of alkali sulfites on the α-halogen acids,[6] the reaction of acetyl chloride with silver sulfate,[7] and the reaction of potassium or ammonium bisulfite with crotonic acid to form α-sulfobutyric acid.[8]

Russell and Cameron[9] have studied the acidity of sulfuric acid in mixtures of acetic anhydride with acetic acid and conclude that acetic anhydride and sulfuric acid react to form an ultra-acidic mixed anhydride which undergoes rearrangement to form sulfoacetic acid, which does not show ultra-acidic behavior. Beer[10] has suggested the formation of a compound designated as "diacetylium sulfate" from which the mixed anhydride of acetic and sulfuric acid can be formed.

In the work of Franchimont,[1] molar ratios of sulfuric acid to acetic anhydride of one to one and one to two were employed and the resulting exothermic reactions were vigorous. In view of the common use of sulfuric acid as a catalyst, it appeared of interest to determine whether sulfuric acid also reacted with anhydrides under the general conditions of esterification reactions and, if so, to ascertain the rate. In these experiments, the reaction of sulfuric acid with acetic, propionic and *n*-butyric anhydrides at various concentrations in the corresponding acids was followed, using low sulfuric acid/anhydride ratios.

Experimental

The aliphatic anhydrides were obtained by distilling C. P. grades and utilizing the following fractions: acetic anhydride 138 to 140°, propionic anhydride 166 to 168°, *n*-butyric anhydride 76 to 78° at 11 mm. Chemically pure grades of the aliphatic acids were employed as the diluents.

Specially designed reaction flasks of the Erlenmeyer type with glass-stoppered side arms through which samples could be removed periodically were used. The flasks were closed with glass stoppers carrying glass bearings through which glass stirrers were introduced. A reaction temperature of 40 ± 0.1° was chosen in order that the reactions would run practically to completion within convenient times.

Stock solutions of sulfuric acid were prepared by diluting 12.5 cc. of 95% sulfuric acid to 250 cc. with the aliphatic acid corresponding to the anhydride to be studied. These were kept in glass-stoppered flasks in the constant temperature bath. Twenty-five cc. portions of the sulfuric acid–aliphatic acid solutions were added to mixtures of calculated amounts of the aliphatic anhydrides and the additional amounts of the aliphatic acids required to produce the desired anhydride concentrations as shown in Table I. The aliphatic acid–aliphatic anhydride mixtures were brought to a temperature of 40° before the sulfuric acid solution was added.

TABLE I

Sulfuric acid–aliphatic acid mixture, cc.	Aliphatic acid, cc.	Aliphatic anhydride, cc.	Designation % anhydride
25	0	225	90
25	37.5	187.5	75
25	100	125	50
25	162.5	62.5	25

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* Presented in part before the Division of Physical and Inorganic Chemistry at the Milwaukee Meeting of the American Chemical Society, September 5–9, 1938.

(1) Franchimont, *Compt. rend.*, **92**, 1054 (1881); *Rec. Trav. Chim.*, **7**, 27 (1888).

(2) Franchimont and Backer, *Akad. Amsterdam Versl.*, **23**, I, 648 (1914); *Chem. Zentr.*, **85**, II, 1391 (1914).

(3) Melsens, *Ann.*, **52**, 276 (1844).

(4) Baumstark, *ibid.*, **140**, 81 (1866).

(5) Carl, *Ber.*, **14**, 64 (1881).

(6) Collmann, *Ann.*, **148**, 109 (1868); Hemilian, *ibid.*, **168**, 145 (1873).

(7) Kammerer and Carius, *ibid.*, **131**, 165 (1864).

(8) Beilstein and Wiegand, *Ber.*, **18**, 483 (1885).

(9) Russell and Cameron, THIS JOURNAL, **60**, 1345 (1938).

(10) Beer, Dissertation, Leipzig, 1927.

In the percentages shown, no correction is made for any change in volume due to mixing.

As soon after mixing as possible, duplicate 5-cc. samples were removed for determination of the sulfuric acid content at the start of the experiments. Additional duplicate samples were removed at the designated periods of time and analyzed to determine the amount of precipitable sulfate ion present. The 5-cc. samples were added to approximately 200 cc. of distilled water containing 4 cc. of 6 *N* hydrochloric acid. The solutions were heated to boiling and the sulfate ion precipitated with 10 cc. of 10% barium chloride solution. The barium sulfate was digested in the usual manner, isolated, ignited and weighed. The barium salts of the sulfoaliphatic acids are comparatively soluble in water and were not precipitated under the conditions employed. The mixed anhydrides of the aliphatic acids with sulfuric acid quickly decomposed in the presence of water to form the corresponding acids.

In order to determine whether sulfuric acid would react with the aliphatic acid, a solution of sulfuric acid in acetic acid was prepared of approximately the concentration used in these experiments and allowed to stand for eleven days at room temperature. Samples removed at the beginning and at the end of this period gave analytical values of 0.0417 and 0.0416 g. sulfuric acid per 5 cc., respectively, which indicated that little if any sulfoacetic acid was formed.

TABLE II

50% ANHYDRIDE–50% ACID

Time	H_2SO_4 G./5 cc.	K^1/Min.$^{-1}$
	Acetic anhydride	
2 min.	0.0416	
15 min.	.0401	0.0030
30 min.	.0399	.0015
1 hr.	.0379	.0016
3 hr.	.0304	.0018
7.5 hr.	.0184	.0018
24 hr.	.0033	.0018
32 hr.	.0015	.0017
	Av.	.0019
	Propionic anhydride	
2 min.	0.0380	
30 min.	.0354	0.0025
1 hr.	.0344	.0017
2 hr.	.0318	.0015
5 hr.	.0264	.0012
8 hr.	.0224	.0011
24 hr.	.0087	.0010
32 hr.	.0058	.00098
48 hr.	.0022	.00099
56.5 hr.	.0013	.0010
72 hr.	.0001	.0014
	Av.	.0013
	n-Butyric anhydride	
2 min.	0.0380	
1.2 hr.	.0287	0.0040
2.2 hr.	.0245	.0034
5.1 hr.	.0160	.0029
8 hr.	.0104	.0027
23 hr.	.0005	.0031
	Av.	.0032

The experimental results obtained using 50% concentrations of the three anhydrides are tabulated in Table II. In order to conserve space, the analytical data for the other anhydride concentrations are not included.

The analytical results are expressed in terms of sulfuric acid though they include the sulfate which may be present as acetyl sulfuric as well as free sulfuric acid. In these experiments we are interested in the amount of sulfuric acid which has been converted into the sulfoaliphatic acid and not in the state of the residual sulfate ion. The values given are the averages of duplicate determinations.

When the experimental data are employed in the usual equation for a first-order reaction

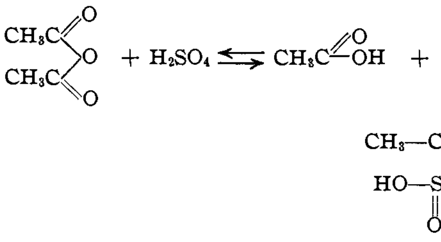
$$k^1 = \frac{1}{t}\, 2.303 \log \frac{a}{a - x}$$

reasonably constant values for k^1 are obtained. In these calculations, a is the amount of precipitable sulfate ion at the start of the experiment and $a - x$ is the amount of precipitable sulfate ion at time t. The average k^1 values for the various experiments are tabulated in Table III.

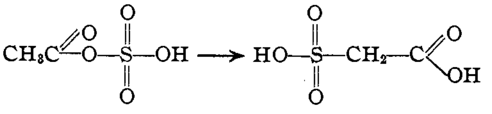
Discussion

Since the principal purpose of the work was to demonstrate the disappearance of sulfuric acid under conditions which simulate those prevailing in esterification reactions, the rate measurements were necessarily made over a very wide range of solvent conditions. For this reason, it is impossible to draw, in some particulars, rigorous conclusions concerning the mechanism of reaction. In spite of this fact, it is believed that a reasonably accurate formulation of the course of the reaction can be deduced in at least a semi-quantitative manner.

On the basis of independent evidence concerning the same type of reaction, Franchimont[1] and others[9] have postulated the following mechanism for the production of sulfoacetic acid



(1)



(2)

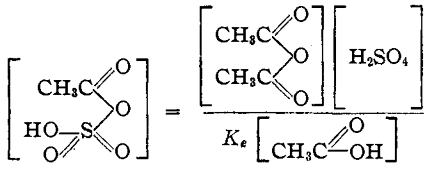
in which equilibrium in reaction (1) is established rapidly, and reaction (2) is the slow or rate-de-

TABLE III

CALCULATED FIRST-ORDER REACTION CONSTANTS

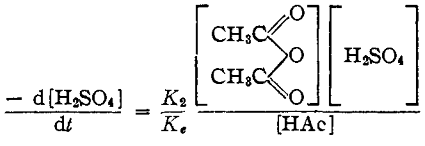
Anhydride, %	Acid, %	Acetic k^1/min.$^{-1}$ (av.)	Acetic Number of k^1 values averaged	Propionic k^1/min.$^{-1}$ (av.)	Propionic Number of k^1 values averaged	n-Butyric k^1/min.$^{-1}$ (av.)	n-Butyric Number of k^1 values averaged
90	10	0.053	3	0.021	4	0.023	5
75	25	.0115	6	.0048	6	.0082	7
50	50	.0019	7	.0013	10	.0032	5
25	75	.00049	15	.00033	12	.00085	10

termining step. By the well-known steady state treatment, the instantaneous concentration of the intermediate, acetylsulfuric acid, is given by the expression



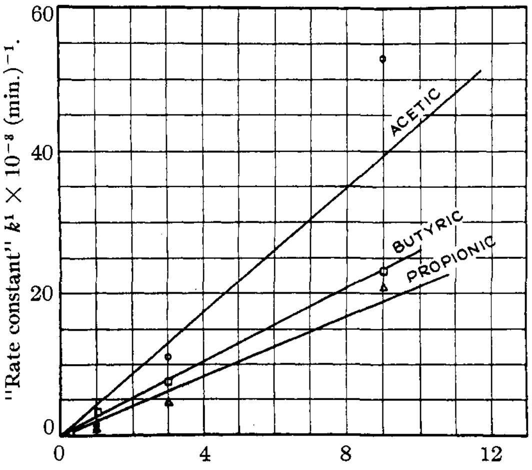
$$[\mathrm{CH_3COOSO_2OH}] = \frac{[(\mathrm{CH_3CO})_2\mathrm{O}][\mathrm{H_2SO_4}]}{K_e\,[\mathrm{CH_3COOH}]} \qquad (3)$$

where K_e is the equilibrium constant in reaction (1). The differential rate expression for the over-all process is thus given as follows



$$\frac{-\,d[\mathrm{H_2SO_4}]}{dt} = \frac{K_2}{K_e}\,\frac{[(\mathrm{CH_3CO})_2\mathrm{O}][\mathrm{H_2SO_4}]}{[\mathrm{HAc}]} \qquad (4)$$

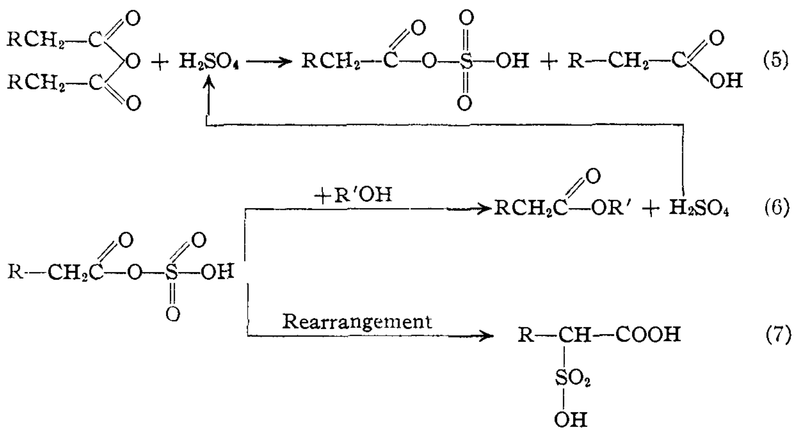
The velocity of the over-all reaction should accordingly be proportional to the first power of the sulfuric acid concentration and to the first power of the ratio Organic anhydride/Organic acid. When the log of $\frac{a}{a-x}$ is plotted against the time, linear relationships are obtained in each experiment. Since the concentration of the anhydride and its hydrate in each case was so much greater than that of the sulfuric acid, only the latter changes appreciably in concentration throughout the course of reaction. Linearity in these relationships indicates that the sulfuric acid concentration enters to the first power as demanded by expression (4). Figure 1, in which the average apparent rate constants of the over-all reaction at various values of anhydride concentration, as tabulated in Table III, are plotted against the ratio Organic anhydride/Organic acid, shows a considerable non-random departure from linearity. The approximation is, however, about as good as can be expected, considering the change in character of the solvent in the four separate measurements. It will be observed, also, from Fig. 1, that the deviations from linearity appear to become less serious with increasing length of the chain attached to the carboxyl group, further suggesting the importance of solvent effects. It thus appears that the data obtained in this investigation are compatible with the mechanism previously proposed and, indeed, appear to afford it considerable substantiation.



Ratio of anhydride to acid.

Fig. 1.

The data indicate that sulfuric acid reacts with the lower aliphatic anhydrides to form sulfoaliphatic acids even when the sulfuric acid is present in the small amounts employed to catalyze acylation reactions. In esterification processes, the reaction which produces sulfoaliphatic acids may proceed concurrently with the esterification reaction, and the rate of disappearance of the sulfate ion should depend on the original concentration of the anhydride in the reaction mixture as well as the rate at which the anhydride is withdrawn from the reaction by esterification. Since the mixed anhydride of sulfuric acid and the aliphatic acid appears to be formed quickly in esterification mixtures,[9] this compound may be the active acylating agent in many reactions as was suggested by Franchimont.[1] The possible mechanism is indicated in the following series of reactions.



The mixed anhydride of sulfuric and the aliphatic acid may react with the material to be acylated, liberating a molecule of sulfuric acid which again may react with a molecule of aliphatic anhydride, and the acylation cycle may be repeated or the mixed anhydride may rearrange to a sulfoaliphatic acid, thus removing the sulfuric acid from further participation in the acylation.

The authors wish to express their appreciation to Dr. William J. Priest of these Laboratories for his assistance in the kinetic interpretation of these data.

Summary

The rate of formation of sulfoaliphatic acids by reaction of sulfuric acid with aliphatic anhydrides at 40° has been measured, using small amounts of sulfuric acid in various concentrations of acetic, propionic and *n*-butyric anhydrides in the corresponding acids.

The rate of disappearance of sulfate ion follows the first-order reaction equation and is related to the concentration of the aliphatic anhydride. The relation between the experimental results and the mechanism of the reaction is discussed.

A mechanism of acylation in the presence of sulfuric acid catalyst is suggested.

ROCHESTER, N. Y. RECEIVED FEBRUARY 19, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Diene Addition Products to Diaroylethylenes and their Transformation Products. II

BY ROGER ADAMS AND R. B. WEARN[1]

In a recently published article[2] it was shown that butadiene, 2,3-dimethylbutadiene and cyclopentadiene undergo an essentially quantitative addition to dibenzoylethylene with formation of dibenzoylcyclohexenes (I). Syntheses from these adducts were developed for the corresponding dibromo addition products (II), dihydroisobenzofurans (V), isobenzofurans (IV), *o*-dibenzoylbenzenes (VI), oxido-tetrahydronaphthalenes (VII) and substituted naphthalenes (VIII). A comparison of the procedures used with those previously known for the same compounds was discussed. The series of reactions is illustrated by formulas I–VIII.

In this paper, analogous reactions between the *trans* forms of di-*p*-chlorobenzoyl, di-*p*-toluyl and dimesitoyl ethylenes and butadiene, 2,3-dimethylbutadiene and cyclopentadiene are reported in order to demonstrate the extent of applicability of these methods in preparative work Butadiene and cyclopentadiene added quantitatively to all three of the diaroyl ethylenes with formation of 4,5-diaroyl cyclohexenes (I). 2,3-Dimethylbutadiene also added to all except the dimesitoylethylene. Apparently, in this case, steric influences prevent the addition from taking place.

The cyclopentadiene addition products could in no case be converted to furans, possibly on account of the strains involved. Similarly, the dimesitoylethylene and butadiene adduct did not form a furan, due probably to steric influences.

The reactions discussed below, except for the addition of bromine to the original adducts, the 4,5-diaroyl cyclohexenes (I), apply merely to the products formed from di-*p*-chlorobenzoylethylene and di-*p*-toluylethylene with butadiene and 2,3-dimethylbutadiene.

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[1] An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Adams and Gold, THIS JOURNAL, **62**, 56 (1940). See also Adams and Geissman, *ibid.*, **61**, 2083 (1939).