cis-4,5-Dimethylthiazolidine-2-thione.—A mixture of 1 g. of *trans*-2,3-butylenimine[21] and 2 g. of carbon disulfide was sealed in a glass ampoule and heated at 100° for 5 hr. The contents of the ampoule were dissolved in hot 10% aqueous sodium hydroxide solution. The solution was decolorized with charcoal, filtered, and cooled. Acidification with hydrochloric acid precipitated the colorless thiazolidinethione: The crude product was recrystallized from benzene–cyclohexane: yield, 0.70 g. (34%). In like manner, *trans*-4,5-dimethylthiazolidine-2-thione was prepared in 49% yield from *cis*-2,3-butyleneimine.[21]

The Reactions of β-Aminoalkyl Hydrogen Sulfates. II. The Reaction of Sodium β-Aminoalkyl Sulfate with Potassium Ethyl Xanthate[1]

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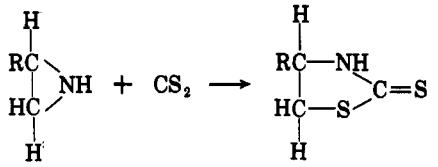
Received September 11, 1964

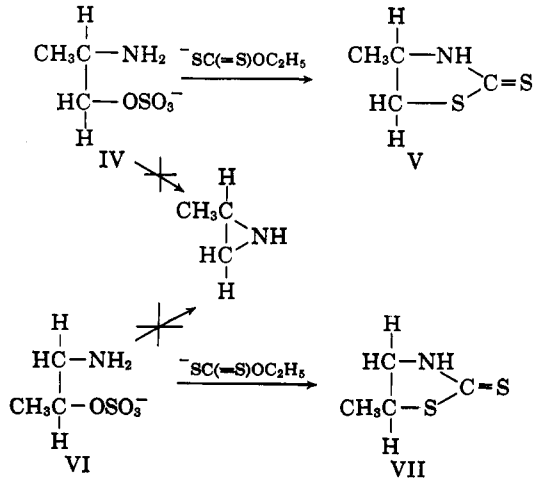
The kinetics of the reaction of sodium β-aminoethyl sulfate (I) and its α- and β-alkyl derivatives with potassium ethyl xanthate to give thiazolidine-2-thiones (II) have been studied. The rate-controlling step is the first-order decomposition of the ethyl xanthate anion to give carbon disulfide which reacts with I to give a dithiocarbamate intermediate III. The latter is converted to II by an intramolecular displacement of the sulfate group by the dithiocarbamate group. A competing reaction, the intramolecular displacement of the sulfate group of I by the neighboring amino group, gives aziridine which reacts with potassium ethyl xanthate and gives II. The two paths to II are not stereochemically equivalent.

Sodium β-aminoethyl sulfate and potassium ethyl xanthate (KEX) react to give thiazolidine-2-thione. The stoichiometry and scope of the reaction have been covered in the accompanying paper.[3] The purpose of this paper is to report on the observed kinetics and to propose a mechanism consistent with the kinetics, stoichiometry, and stereochemistry of the reaction.

Aziridines are opened by carbon disulfide giving thiazolidine-2-thiones.[4] Ring opening of 2-alkylaziridines occurs between the nitrogen and least-substituted carbon atom to give 4-alkyl-thiazolidine-2-thiones.[4b] The reaction of the β-aminoalkyl sulfate anion (I) with potassium ethyl xanthate (KEX) did



not appear to proceed through the aziridine intermediate since the product from sodium 2-aminopropyl sulfate (IV) and KEX was 4-methylthiazolidine-2-thione (V) while that from sodium 1-amino-2-propyl sulfate (VI) was 5-methylthiazolidine-2-thione (VII).[3] Similar results were observed in the preparation of the 4-ethyl, 5-ethyl, 4-phenyl, and 5-phenyl thiazolidines.[3]



Results and Discussion

In an attempt to uncover the mechanism of the reaction, the rate constants of three reactions were determined: (A) the formation of aziridine from sodium 2-aminoethyl sulfate (I) in aqueous alkali; (B) the decomposition of potassium ethyl xanthate (KEX) in alkaline solution; and (C) the formation of thiazolidine-2-thione (II) from I and KEX. A reaction temperature of 75° was chosen solely for convenience so that a kinetic run could be completed in a reasonable period. The data for the three reactions are summarized in Table I.

TABLE I

THE DECOMPOSITION OF SODIUM 2-AMINOETHYL SULFATE AND POTASSIUM ETHYL XANTHATE

Reaction	[I], *M*	[KEX], *M*	[NaOH], *M*	10^3 *k* (min.$^{-1}$)
A	0.5	...	0.5	0.48 ± 0.01
B	...	1×10^{-4}	pH 8	4.3 ± 0.3
B	...	1×10^{-4}	pH 9	4.9
B	...	1×10^{-4}	pH 10	8.7 ± 0.3
C	0.5	0.5	...	3.62 ± 0.07[a] (3.34)[b]
C	0.5	1.0	...	2.86[a]
C	1.0	0.5	...	3.14[a]

[a] Calculated from rate of disappearance of I. [b] Calculated from rate of formation of thiazolidine-2-thione.

The formation of aziridine from I was carried out in an equivalent amount of 0.5 *N* sodium hydroxide. The reaction was followed by determining the decrease in concentration of hydroxide ion as a function of time. The reaction is first order in I and zero order in hydroxide ion. The results of a typical run are shown in Figure 1.

(1) (a) From the Ph.D. Thesis of R. A. Bafford, University of Maryland, June 1960. (b) Presented at the 148th National Meeting of the American Chemical Society, Sept. 1964, Abstracts, p. 42S.

(2) To whom inquiries should be addressed at Lucidol Division, Wallace and Tiernan, Inc., 1740 Military Rd., Buffalo, N. Y. 14240.

(3) C. S. Dewey and R. A. Bafford, *J. Org. Chem.*, **30**, 491 (1965).

(4) (a) S. Gabriel and H. Ohle, *Ber.*, **50**, 840 (1917); (b) L. Clapp and J. Watjen, *J. Am. Chem. Soc.*, **75**, 1490 (1953).

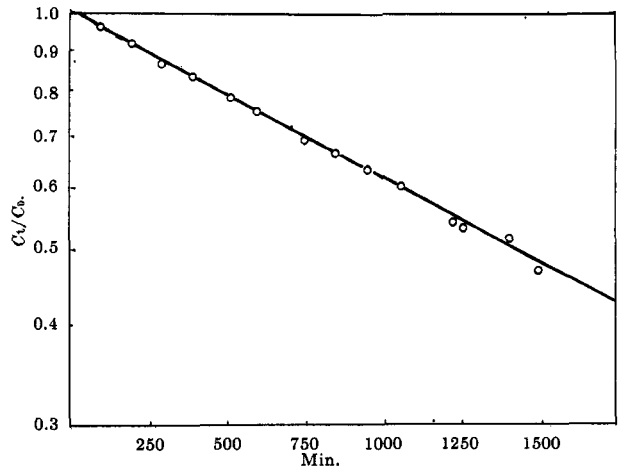


Figure 1.—The reaction of sodium 2-aminoethyl sulfate with sodium hydroxide at 75°; C_t = M of sodium 2-aminoethyl sulfate.

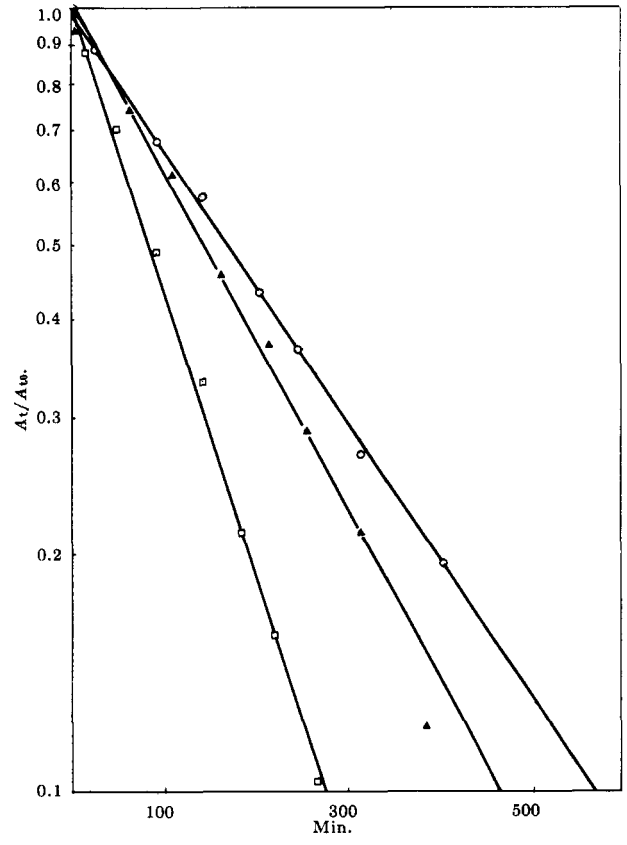


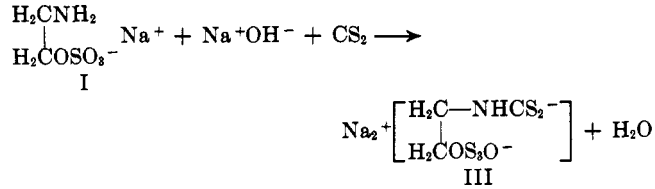
Figure 2.—The decomposition of potassium ethyl xanthate in alkaline buffer at 75°; ○ = pH 8, ▲ = pH 9, and □ = pH 10.

Reaction B, the decomposition of KEX, was carried out in solutions buffered at pH 8, 9, and 10. The decomposition was followed by measuring the absorbance at 301 mμ as a function of time. The procedure was that of Iwasaki and Cooke who studied the reaction in acidic buffers.[5] Typical results are shown in Figure 2. The data (Table I) approximately fit the following equation, $k_1 = k_1' + k_1''[OH^-]$, where k_1 is the experimentally determined first-order rate constant at a given pH, k_1' is the rate constant for the pH independent decomposition, and k_1'' is the second-order constant for the alkali-catalyzed decomposition. At 75°, $k_1' = (4.3 \pm 0.3) \times 10^{-3}$ min.$^{-1}$ and $k_1'' = 43 \pm 3$ l. mole^{-1} min.$^{-1}$.

The specific rate constant and kinetic order for the reaction of I with KEX (reaction C) at 75° were calculated from data obtained by two independent procedures: (1) the rate of disappearance of I and (2) the rate of formation of the product, II. The reaction was first order over-all, first order in ethyl xanthate ion, and zero order in aminoethyl sulfate anion. The pH of the reaction medium decreased from 10.1 at 5% conversion to 9.6 at 75% conversion. Thus rate data for reaction C has been compared with that obtained from reaction B in buffered solutions of pH from 8 to 10. Correlation of the rate data for the two reactions is considered very good in view of the fact that reagent concentrations in the two reactions differ by a factor of 10^4. A comparison of the rate constants for reactions A and C indicates that II is formed at least seven times faster than I is converted to the aziridine.

(The difference between the rates of the two competing reactions is actually greater than a factor of seven at pH 10. At this pH, about 10% of I is protonated, thus the actual initial concentration of I available for reaction A is 0.45 M. Reaction C is zero order with respect to I.)

When the reaction between I and KEX was carried out in 95% ethanol, an amorphous solid precipitated from the reaction mixture. The reactants, I and KEX, and the product, II are soluble in 95% ethanol. An aqueous solution of the amorphous solid (III) liberated carbon disulfide when acidified and did not give a precipitate when treated with aqueous barium chloride solution. When an aqueous solution of III was refluxed for several hours, II and sodium sulfate were formed. Although III could not be purified for elemental analysis, its chemical properties were identical to those of the dithiocarbamate salt of I prepared by adding an ethanolic solution of carbon disulfide to an ethanolic solution containing equimolar amounts of I and sodium hydroxide. The precipitation of III occurred within 15 sec. of mixing the two solutions at room temperature. Prior formation of sodium ethyl xanthate is not involved since there is no reaction between I and sodium ethyl xanthate at room temperature.



It is therefore postulated that the reaction under study proceeds by the following steps: (1) the first-order decomposition of KEX to carbon disulfide and potassium ethoxide; (2) rapid reaction of carbon disulfide with I to give III; and (3) an intramolecular nucleophilic displacement of the sulfate group by the dithiocarbamate group to give II. However, II can also be formed from KEX and the aziridinium ion (reaction 5) which is produced by the competing reaction 4.

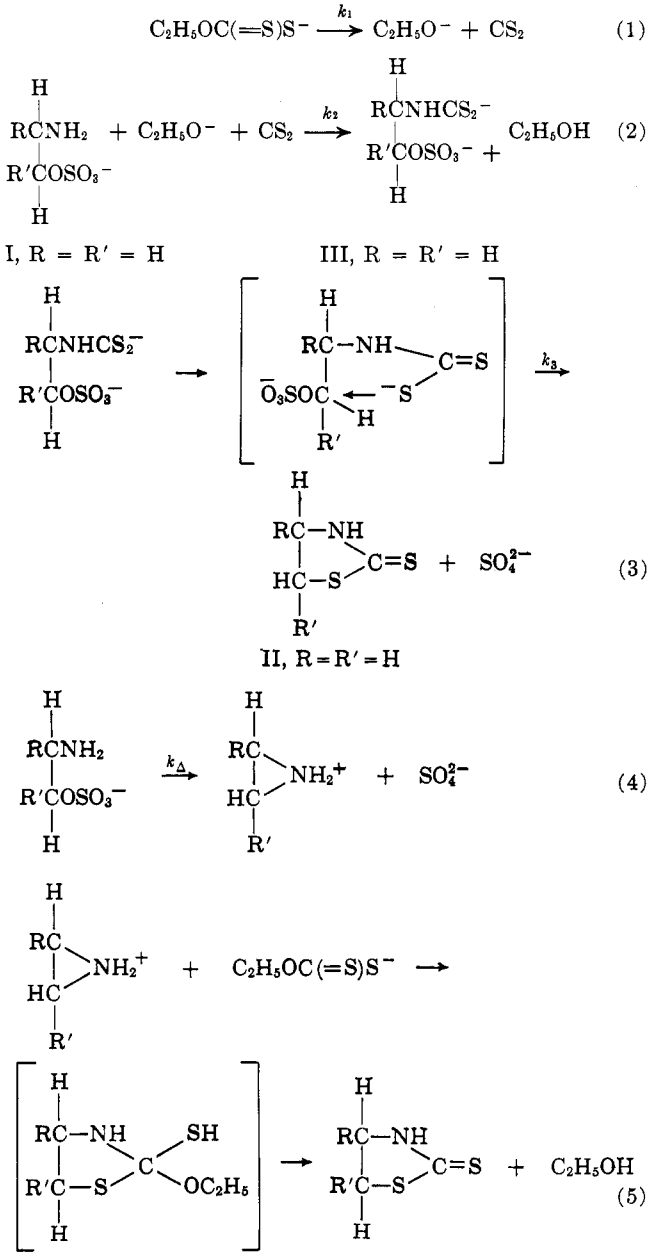
(5) J. Iwasaki and S. Cooke, *J. Am. Chem. Soc.*, **80**, 285 (1958).

TABLE II

RATE CONSTANTS FOR THE REACTION OF SODIUM 2(1)-ALKYL-β-AMINOETHYL SULFATE WITH POTASSIUM ETHYL XANTHATE

Compd.	Substituent	10^3k_1 (min.$^{-1}$) Method 1[a]	10^3k_1 (min.$^{-1}$) Method 2[b]	10^3k_2 (min.$^{-1}$)[c]	10^3k_Δ (min.$^{-1}$)[d]	pK'_a[e]
I	H	3.62	3.34	..	0.48	8.97 ± 0.01
VIII	1-Methyl	3.73	3.43	..	0.95	8.97 ± 0.02
IX	1-Isopropyl	..	3.20	21.3	0.50	9.18 ± 0.03
XI	1-Benzyl	..	4.27	5.2	0.24	8.90 ± 0.01
XII	2-Methyl	..	3.12	..	3.10	9.02 ± 0.03
XIII	2-Ethyl	..	...	..	4.41	9.02 ± 0.02
XVIII	2,2-Dimethyl	..	15.1[f]	..	19.5	9.06 ± 0.01
XX	2,3-Trimethylene	..	...	..	10.6	8.89 ± 0.01

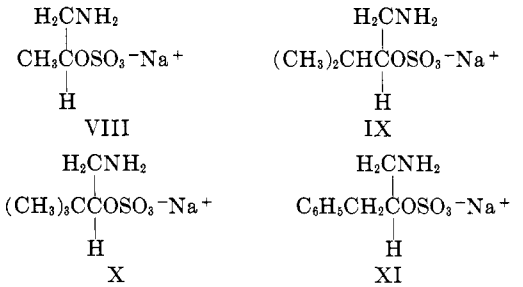
[a] Determined from the rate of disappearance of sodium aminoalkyl sulfate. [b] Determined from the rate of appearance of the thiazolidine-2-thione. [c] Calculated by the "time ratio" method, ref. 7. [d] Rate constants for the formation of the aziridines. [e] Determined by electrometric titration of the aminoalkyl hydrogen sulfate. [f] Calculated from rate of appearance of the product at zero time.



The following relationships exist between the various rate constants: $k_2 >> k_1$ since III is formed almost instantaneously from I and carbon disulfide at room temperature (*vide supra*), $k_3 > k_1$ since rate data based either on disappearance of I or on formation of II gave simple first-order kinetics thus establishing the validity of the steady-state approximation, and $k_1 > k_\Delta$ by experimental observation.

If now the reaction is carried out with alkyl-substituted β-aminoethyl sulfate ions, there are several different relationships between the rate constants (k_2 is always very large in comparison with the other rate constants); see cases 1–3 below. Examples of all three will be discussed in turn.

Case 1. $k_3 \gtrless k_1$, $k_1 > k_\Delta$.—If bulky substituents are placed on the carbon atom from which the sulfate group is displaced, then the rate of formation of the thiazolidine ring *via* intramolecular displacement by the dithiocarbamate group will be retarded (reaction 3, R = H, R′ = alkyl). However, k_1 will be little effected since an alkyl group, R′, will have but minor effect on the basicity of the aminoalkyl sulfate anion and k_1 changes by only a factor of two between pH 8 and 10. Since steric hindrance plays a greater role in the formation of five-membered rings than in the formation of three-membered rings,[6] alkyl substituents at the site of displacement will have a greater effect on k_3 than on k_Δ. The following compounds were found to fit into this category: sodium 1-amino-2-propyl sulfate (VIII), sodium 1-amino-3-methyl-2-butyl sulfate (IX), sodium 1-amino-3,3-dimethyl-2-butyl sulfate (X), and sodium 1-amino-3-phenyl-2-propyl sulfate (XI). These compounds with KEX gave the 5-alkylthiazolidine-2-thiones.[3]



The reaction of VIII with KEX followed a simple first-order law over two half-lives. However neither IX nor XI upon reaction with KEX followed a simple rate law and both had measurable induction periods (Figure 3). The steady-state approximation is no longer valid and the kinetics are those for two consecutive first-order reactions. The rate constants were evaluated using the "time ratio" method.[7] The

(6) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 163.

(7) A. Frost and R. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 158.

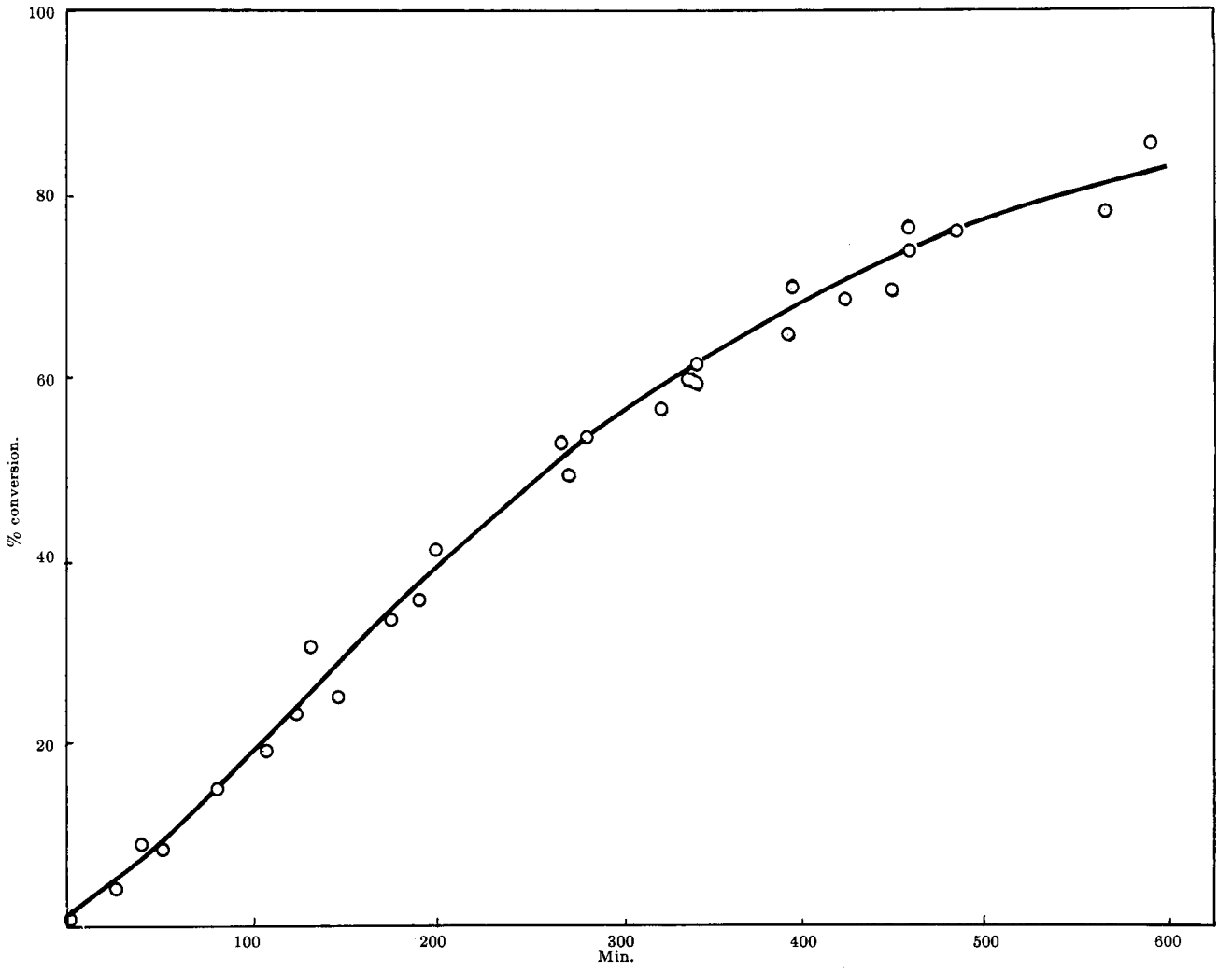


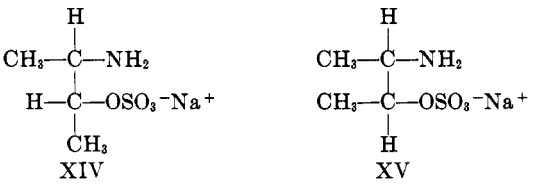
Figure 3.—The reaction of sodium 1-amino-3-methyl-2-butyl sulfate with potassium ethyl xanthate at 75°.

reaction of X with KEX showed a definite induction period but experimental data were too scattered for determination of rate constants. The data are summarized in Table II. It will be noted that k_Δ also decreased as the size of the alkyl group increased.

Case 2. $k_3 > k_1$, $k_1 \simeq k_\Delta$.—When alkyl substituents are attached to the nitrogen-bearing carbon atom of sodium 2-aminoethyl sulfate, cyclization to the corresponding aziridine is more facile and k_Δ is larger (reaction 4, R = alkyl, R′ = H). If k_Δ is of the same order of magnitude as k_1, formation of the thiazolidine will occur *via* two paths: (1) intramolecular displacement of the sulfate group by the dithiocarbamate group which has already been discussed and (2) reaction of the aziridinium ion with potassium ethyl xanthate.

Since the aziridine ring opens between the nitrogen and least-substituted carbon, the product of reaction 5 will be a 4-alkylthiazolidine-2-thione.

As shown in Table II, k_Δ for sodium 2-aminopropyl sulfate (XII) and for sodium 2-aminobutyl sulfate (XIII) are about equal to k_1—therefore product is formed *via* both reaction paths—but both give only the 4-alkyl thiazolidinethiones. However, the stereochemistry of the two paths is different. Reactions 1–3 involve a single inversion of configuration (displacement of the sulfate by the dithiocarbamate group). Reactions 4–5 involve two inversions (displacement of the sulfate by the amino group and the *trans* opening of the aziridine). This was demonstrated with the sodium *threo*- and *erythro*-2-amino-3-butyl sulfates, (*threo*, XIV) and (*erythro*, XV).



When either of these salts was treated with the stoichiometric quantity of KEX a mixture of the *cis*-4,5-dimethylthiazolidine-2-thione (XVI) and the *trans* compound XVII was obtained.[8] If the product was formed by reactions 1–3, XIV would give XVI while XV would give XVII. Reactions 4–5 involve two inversions; thus XIV would give XVII and XV would give XVI. (See Scheme I.)

As predicted by the mechanism, the use of an excess of KEX lead to a predominance of the single inversion product. The data are summarized in Table III.

Case 3. $k_3 > k_1$, $k_\Delta > k_1$.—Sodium 2-amino-2-methylbutyl sulfate (XVIII) is converted to 2,2-dimethylaziridine about seven times faster than KEX is decomposed to carbon disulfide (Table II). No simple kinetic equation could be found to fit the rate data for the formation of 4,4-dimethylthiazolidine-2-

SCHEME I

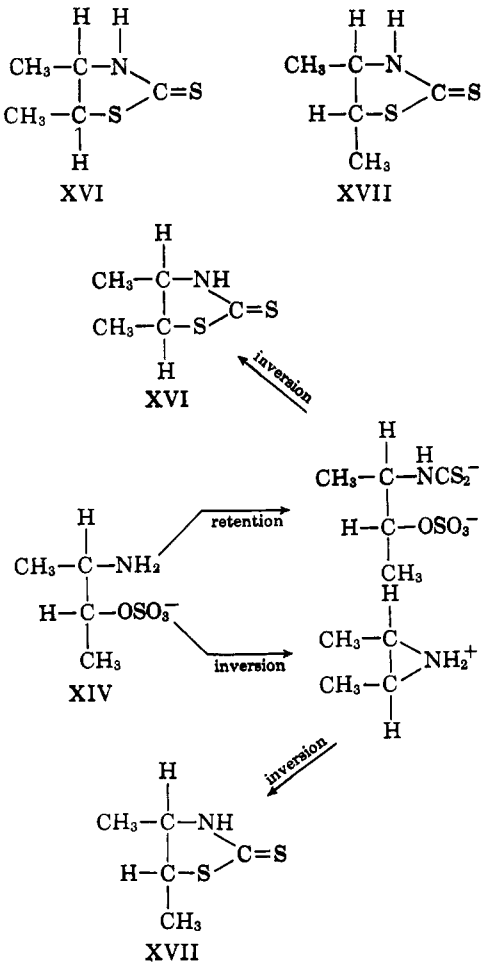


TABLE III

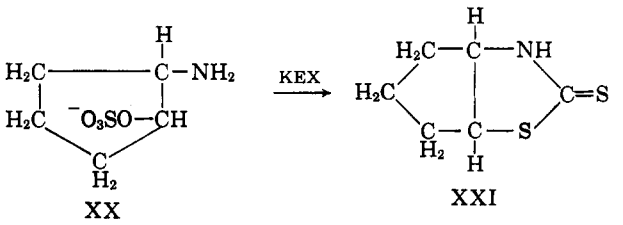
THE REACTION OF SODIUM 2-AMINO-3-BUTYL SULFATE WITH POTASSIUM ETHYL XANTHATE

NaABS[a] configuration	$10^3 k_\Delta$ (min.$^{-1}$)[b]	KEX:NaABS, mole ratio	Product[c] % yield	% composition—*cis*	% composition—*trans*
threo	6.43	1	59	58	42
threo	..	3	78	87	13
erythro	8.18	1	52	35	65
erythro	..	3	74	5	95

[a] Sodium 2-amino-3-butyl sulfate. [b] Rate constants for the formation of the aziridines. [c] 4,5-Dimethylthiazolidine-2-thione.

thione (XIX) from XVIII and KEX. However, XIX was formed faster than KEX decomposed. The initial rate of formation of XIX approximated the rate of formation of 2,2-dimethylaziridine from XVIII (Table II). Thus KEX, while failing to react with the aminoalkyl sulfates, is capable of reacting rapidly with aziridinium ions to form an intermediate which is readily converted to the thiazolidine-2-thione.

A somewhat different result was observed for sodium *trans*-2-aminocyclopentyl sulfate (XX). Although k_Δ for XX is four times greater than k_1, the only product of the reaction with KEX was a poor yield (11%) of 2-thia-4-aza-*cis*[3.3.0]bicyclooctane-3-thione (XXI). This must be formed *via* reactions 1–3. The *trans* compound which would be expected from cyclopentenimine and carbon disulfide or KEX is apparently too strained to exist although the corresponding compound has been prepared from cyclohexenimine.[8] No identifiable products were obtained from the reaction of cyclopentenimine with carbon disulfide.



Experimental

Reagents.—The preparation, purification and identification of all reactants and products have been reported.[3]

Kinetic Runs.—β-Aminoalkyl hydrogen sulfate (0.025 mole) was dissolved in 25 ml. of 1.00 *N* sodium hydroxide solution. Potassium ethyl xanthate (4.010 g., 0.025 mole) was then added and the reaction mixture was diluted to 50 ml. with distilled water. Aliquots (5 ml.) were placed in glass ampoules which were sealed and placed in a constant temperature bath at 75 ± 0.04°. Ten minutes was allowed for the ampoules to equilibrate with the bath before the timer was started. Ampoules were periodically removed from the bath and dropped into a Dry Ice–isopropyl alcohol mush to quench the reaction.

When rate constants for the formation of aziridines from sodium aminoalkyl sulfates were to be determined, 0.025 mole of the β-aminoalkyl hydrogen sulfate was dissolved in sufficient 0.1 *N* NaOH to give 50 ml. of solution.

Evaluation of Rate Constants. A. The Reaction of Potassium Ethyl Xanthate and Sodium Aminoalkyl Sulfate. Rate of Disappearance of Sodium Aminoalkyl Sulfate.—The contents of the ampoule were transferred to a beaker and diluted with distilled water. The unchanged sodium aminoalkyl sulfate was titrated with 0.1 *N* hydrochloric acid. The titration was followed with a Beckman Model G pH meter. Titrations were carried out as rapidly as possible to avoid acid-catalyzed decomposition of unchanged KEX.

A plot of log C_t/C_0 (where C_t is the concentration of sodium aminoalkyl sulfate at time t and C_0 is the initial concentration) *vs.* time was used to determine the rate constant. The plots were linear over at least two half-lives for all rate constants reported. Some typical data are shown in Table IV.

TABLE IV

THE REACTION OF SODIUM 2-AMINOETHYL SULFATE WITH POTASSIUM ETHYL XANTHATE[a] AT 75°

Run A6 Time, min.	Run A6 0.1 *N* HCl, ml.[b]	Run A6 C_t/C_0	Run A8 Time, min.	Run A8 0.1 *N* HCl, ml.[b]	Run A8 C_t/C_0
0[c]	24.75	0.990	0[c]	24.43	0.977
41	21.76	0.870	34	22.20	0.888
99	18.85	0.754	73	19.39	0.776
152	14.70	0.588	116	16.61	0.664
196	12.60	0.504	155	14.40	0.576
252	10.18	0.407	210	11.80	0.472
321	7.68	0.307	259	9.72	0.389
404	5.00	0.200	305	7.72	0.309
455	4.30	0.172	356	7.00	0.280

[a] Reaction mixture: 3.525 g. (0.025 mole) of 2-aminoethyl hydrogen sulfate, 25.00 ml. (0.025 equiv.) of 1.000 *N* sodium hydroxide, 4.010 g. (0.025 mole) of potassium ethyl xanthate, and distilled water to give 50.0 ml. of solution. [b] Volume required to neutralize a 5.00-ml. aliquot of reaction mixture. [c] "Zero" time was 10 min. after first ampoule was placed in thermostat.

Rate of Formation of Thiazolidine.—The contents of the ampoule were transferred to a beaker containing 4 ml. of acetic acid, 1 ml. of hydrochloric acid, and about 40 ml. of distilled water. The beaker was heated in a water bath until its contents had evaporated to dryness. The residue was extracted five times

(8) F. Winternitz, M. Mousseron, and R. Dennilauler, *Bull. soc. chim France*, 1228 (1956).

with 5–8-ml. portions of hot benzene. The filtered benzene extracts were allowed to evaporate at room temperature and the residue was dried to constant weight (±0.5 mg.) in a vacuum desiccator.

The only nonvolatile, benzene-soluble component of the reaction mixture was the thiazolidine. Products isolated in this manner melted from 2 to 8° lower than analytically pure samples.

The data from several runs (Table V) were combined and conversion to thiazolidine was plotted against time. A curve was fitted to the points. Points from this curve were used to plot log $(1 - C_t/C_{00})$ *vs.* time (C_t = conversion at time t and C_{00} = conversion after five half-lives).

TABLE V

THE REACTION OF SODIUM 2-AMINOETHYL SULFATE WITH POTASSIUM ETHYL XANTHATE[a] AT 75°

Run A21			Run A22		
Time, min.	Thiazolidine-2-thione[b]	Conversion, %	Time, min.	Thiazolidine-2-thione[b]	Conversion, %
0	0.0157	5.3	0	0.0094	3.1
31	0.0348	11.7	68	0.0528	17.7
107	0.0854	28.6	134	0.1000	33.2
158	0.1136	38.2	209	0.1352	45.5
237	0.1327	44.6	284	0.1639	55.2
301	0.1679	56.4	354	0.1822	61.2
384	0.1880	63.2	433	0.1974	66.4
439	0.2037	68.4	1403	0.2584	87.0
499	0.2174	73.0			

[a] Reaction mixture: 3.525 g. (0.025 mole) of 2-aminoethyl hydrogen sulfate, 25.00 ml. (0.025 equiv.) of 1.000 *N* sodium hydroxide, 4.010 g. (0.025 mole) of potassium ethyl xanthate, and distilled water to give 50.0 ml. of solution. [b] Grams of thiazolidine-2-thione from 5.00-ml. aliquot of reaction mixture.

B. The Formation of Aziridines from Sodium β-Aminoalkyl Sulfates. Rate of Disappearance of Sodium β-Aminoalkyl Sulfate.—From the stoichiometry of the reaction it can be seen that 1 mole of hydroxyl ion is consumed for each mole of aziridine formed. The contents of each ampoule were titrated with 0.1 *N*

$$H_2NCH_2CH_2OSO_3^- + OH^- \longrightarrow \underset{\diagdown\,\diagup}{\overset{CH_2-CH_2}{\underset{N}{\underset{H}{}}}} + SO_3^{2-} + H_2O$$

sulfuric acid to a pH 4 end point. If C_0 = initial concentration of sodium β-aminoalkyl sulfate, x_0 = ml. of 0.1 *N* acid required to neutralize a 5-ml. aliquot of freshly prepared reaction mixture, x_t = ml. of 0.1 *N* acid required at time = t_t, and C_t = concentration of sodium β-aminoalkyl sulfate at time = t, then $C_t = C_0 - (x_0 - x_t)/50$. Some selected data is shown in Table VI. Plots of log C_t/C_0 *vs.* t were linear for all compounds reported. Reactions were followed through at least two half-lives when the half-life was less than 12 hr. All others were run at least 24 hr. After about 30-hr. etching of the glass ampoules by the sodium hydroxide was severe enough to cause scattering of the points.

The Decomposition of Potassium Ethyl Xanthate in Alkaline Buffer Solutions.—Potassium ethyl xanthate (4.0 mg., 2.5×10^{-5} mole) was dissolved in 250 ml. of the appropriate buffer solution. Aliquots (5.00-ml.) of the mixture were heated in sealed ampoules at 75 ± 0.04° in an oil bath. Ampoules were periodically removed and quenched in a Dry Ice–isopropyl alcohol mush. The sample was transferred to a 1-cm.-path-length quartz cuvette and its absorbance at 301 mμ was measured on a Cary Model 14M spectrophotometer.

TABLE VI

THE FORMATION OF AZIRIDINE FROM SODIUM 2-AMINOETHYL SULFATE[a] AT 75°

Run A34			Run A35		
Time, min.	0.1 *N* H_2SO_4,[b] ml.	C_t/C_0	Time, min.	0.1 *N* H_2SO_4, ml.	C_t/C_0
..	47.70[c]	...	757	39.98	0.691
95	46.79	0.964	854	39.35	0.666
198	45.60	0.918	957	38.55	0.634
302	44.41	0.868	1057	37.70	0.600
401	43.54	0.834	1142	37.05	0.574
517	42.34	0.786	1235	36.21	0.540
603	41.56	0.754	1262	36.04	0.534
1403	35.48	0.511			
1501	34.50	0.472			

[a] Reaction mixture: 3.525 g. (0.025 mole) of 2-aminoethyl hydrogen sulfate and sufficient 1.000 *N* sodium hydroxide to give 50.0 ml. of solution. [b] Volume of acid required to neutralize a 5.00-ml. aliquot. [c] Volume of acid required to neutralize 5.00 ml. of freshly prepared reaction mixture.

A plot of log A_t/A_0 (where A_t = absorbance at time t and A_0 = absorbance at zero time) against time was linear over at least two half-lives of the reaction (Figure 2).

The Determination of Acidity Constants (pK_a') of Aminoalkyl Hydrogen Sulfates.—The acid dissociation constant of each aminoalkyl hydrogen sulfate was determined by electrometic titration using a Beckman Model G pH meter. The following equation was used where N = normality of the base, v = ml. of

$$pK_a = pH - \log \frac{\left\{\frac{Nv}{v_0 + v} + [H^+] + [OH^-]\right\}}{\left\{\frac{a - Nv}{v_0 + v} - [H^+] + [OH^-]\right\}} - \log \frac{f_{A^-}}{f_{HA^\pm}}$$

added base, a = millimoles of aminoalkyl hydrogen sulfate in v_0 ml. of solution. The last term of the equation was neglected because of the difficulty in estimating the activity coefficient factor.[9]

Except near the end point, a more simplified expression, below, was used. Typical results are shown in Table VII.

$$pK_a' = pH - \log \frac{Nv}{a - Nv}$$

TABLE VII

ELECTROMETRIC TITRATION OF 2-AMINOETHYL HYDROGEN SULFATE[a]

Titrant, ml.	pH	pK_a'
0.50	7.72	8.99
1.00	8.03	8.96
2.00	8.39	8.99
3.00	8.61	8.98
4.00	8.79	8.97
5.00	8.98	8.98
6.00	9.15	8.97
7.00	9.32	8.96
8.00	9.54	8.95
9.00	9.81	8.90

[a] Acid, 0.1412 g. (1.0 mmole) of 2-aminoethyl hydrogen sulfate in 100 ml. of distilled water; titrant, 0.100 *N* soduim hydroxide solution.

(9) S. Glasstone, "Introduction of Electrochemistry," D. Van Nostrand, Inc., New York, N. Y., 1942, p. 24.