evidence for inhibition by nitric oxide appears unambiguous.

2. Another not unreasonable explanation would be that the catalytic effect of nitric oxide may be only an indirect one. In the decomposition of ketones appreciable quantities of unsaturated hydrocarbons are produced. It has been amply demonstrated that these compounds can inhibit free radical chain reactions. The normal, "uninhibited" decomposition of these ketones, then, may simply represent the rate of a reaction which is already partially inhibited by these olefinic product molecules. Nitric oxide molecules, in the presence of methyl radicals, may react preferentially with the olefinic inhibitor and thereby enable the chains to increase to their normal length, with a resulting increase in the rate. While many experimental examples can be offered to support this hypothesis, it is difficult to reconcile this view with the fact that nitric oxide inhibits the diethyl ketone decomposition in the presence of olefins, but also catalyzes the decomposition of acetaldehyde where no olefins occur as products.

3. The catalytic effect of nitric oxide can also be accounted for in yet another way. Certain reactions of aldehydes and ketones in solution occur only when there is a methyl group attached to the carbonyl, *e.g.*, the haloform reactions. It is logical to assume that the peculiar effect of this particular linkage would be also operative, to some extent at least, in the gas phase. The catalyzed reaction, therefore, may involve a complex chemical reaction of nitric oxide at the methyl–carbonyl linkage, rather than with the methyl radicals themselves. The fact that nitric oxide produces catalysis even in the fully inhibited decomposition tends to support this view. Support for this hypothesis is also found in the decompositions of aldehydes and ketones where it is noted that nitric oxide catalyses only those compounds having a methyl–carbonyl bond. Finally, the work of Gantz and Walters[15] on the iodine catalyzed decomposition of ketones reveals that iodine behaves in a manner remarkably similar to that of nitric oxide. It was found that iodine strongly catalyzes the decomposition of acetone and methyl ethyl ketone. Significantly, however, iodine produces only a slight catalysis in the case of diethyl ketone. They interpret their results as indicating that the catalyzed reaction is a complex one involving the chemical reaction of iodine atoms. It seems reasonable, therefore, that the mechanism of the nitric oxide and iodine catalyzed reactions are closely analogous.

Unfortunately, the available experimental data do not enable one to arrive at an unequivocal decision as to which explanation is correct. Each has a certain amount of experimental evidence for support. In the final analysis, experiment alone will decide. Investigations are now being conducted in this laboratory in an effort to obtain unambiguous answers to some of the questions raised and these results will be reported shortly.

Acknowledgment.—The authors gratefully acknowledge the generous support of this research by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

The authors also wish to express their appreciation to Dr. S. S. Friedland and Mr. Henry Katzenstein of the Department of Physics for the mass spectrographic analyses.

[15] G. M. Gantz and W. D. Walters, THIS JOURNAL, **63**, 3412 (1941).

STORRS, CONNECTICUT

[CONTRIBUTION FROM THE INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY AND CENTER OF NUCLEAR CHEMISTRY, UNIVERSITY OF PADOVA]

Kinetics of Displacement Reactions at the Sulfur Atom. I. Isotopic Exchange between Sulfite and Alkylthiosulfates

BY ANTONINO FAVA AND GASTONE PAJARO

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The kinetics of the isotopic displacement of sulfite from some alkyl thiosulfates have been studied. The reaction is first order with respect to both reagents and it may be classified as an S_N2 reaction. The exchange exhibits a strong *p*H dependence which is interpreted as being due to the formation of bisulfite ions. Electrolytes catalyze the exchange. The effect of the addition of NaCl has been studied in the range of ionic strength 0.03 to 0.17. The Brønsted equation is not followed. It has been pointed out that the catalysis is particularly strong when multicharged positive ions are present. The temperature dependence of rate has been determined for the following compounds: ethyl, benzyl, allyl, carboxymethyl thiosulfates and ethane dithiosulfate. Entropies and heats of activation have been evaluated. The free energies of activation for the thiosulfate, trithionate and alkyl thiosulfate exchanges are compared and the possible structure of the activated complex is discussed.

Introduction

In the last fifteen years very important progress has been made in the chemistry of sulfur. Particularly significant are the advances in the field of polythio compounds. Here the achievements are mainly due to the work and conceptions of Olav Foss.[1] As a result of his study a new picture covering the entire field has been drawn. The main features of this picture are: (i) in the polythionic compounds the sulfur atoms are in an unbranched chain; (ii) many of the typical reactions of polythionic compounds (with sulfite, thiosulfate, cyanide, etc.) are nucleophilic substitutions at the sulfur atom and can be interpreted in terms of the base strengths of the displacing and displaced groups. The fundamental soundness of these

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[1] O. Foss, *Det. Kgl. Norske Videnskabers. Skrifter*, 1945, Nr. 2 (1947); *Acta Chem. Scand.*, **3**, 1385 (1949); **4**, 866 (1950).

hypotheses has been tested both by X-ray investigation[2,3] of the structure of some polythionic compounds and by radiochemical studies of the reactions of polythionates with sulfite[4] and with thiosulfate.[5]

The recognition of the typical reactions of the polythionic compounds as displacement reactions makes them particularly interesting. Quite generally they may be formulated as

$$-S-X + Y \longrightarrow -S-Y + X$$

where S is a divalent sulfur atom in a chain (not necessarily a chain of sulfur atoms) and X and Y are nucleophilic reagents such as CN^-, SO_3^{--}, SCN^-, etc. The obvious similarity of these reactions with the well known displacements at the carbon atom makes their kinetic behavior very interesting. However, although the kinetics of the nucleophilic substitutions at the carbon are comparatively well known, it is not so for displacements at the sulfur atom. For the latter case only very few kinetic data are available.[6,7] It is the aim of the present work to obtain quantitative kinetic data about these reactions.

The particular reaction chosen to begin with involves the exchange of a SO_3 group between sulfite and compounds containing the grouping $-S-SO_3^-$. Compounds containing the group $-S-SO_3^-$ that could be used for this purpose (beside thiosulfate itself, which represents a rather extreme case) are polythionates and organic thiosulfates. Polythionates, however, are not suitable for kinetic work. Higher polythionates (S_4 to S_6) undergo with sulfite the well known fast reaction of displacement of thiosulfate which would not permit the observation of the competitive reaction of displacement of sulfite. Only with trithionate, which cannot be further desulfurated, can the isotopic exchange be detected.[8] Even for trithionate, however, the working conditions in which the kinetics may be studied are far from being ideal, as we pointed out in a previous paper.[9] There remain the organic thiosulfates. In a preliminary note[10] the existence of the exchange was reported,

$$S^*O_3^{--} + R-S-SO_3^- \rightleftarrows SO_3^{--} + R-S-S^*O_3^-$$

R being an organic radical. The reaction is measurably fast at room temperature so that the kinetics may be conveniently followed. A further advantage of this reaction is its possibility of being studied in great detail by varying the nature of the organic radical bound to the sulfur atom. It is therefore with this type of reaction that the present paper is concerned.

Experimental

The sodium or potassium salts of the following organic thiosulfates were studied: ethyl, benzyl, allyl and carboxymethyl thiosulfates and ethane dithiosulfate. The carboxymethyl compound was prepared from the chloro derivative, all others from the corresponding bromo derivative.[11–14] All were purified by double crystallization from alcohol and analyzed by determining the total sulfur. Some of these compounds (carboxymethyl thiosulfate and ethane dithiosulfate) are very stable and may be stored unaltered for a long time. Others, especially the allylthiosulfate, slowly decompose in the air so that it is preferable to do the kinetic work with freshly prepared samples.

Radioactive sulfite of high specific activity was prepared by reducing radioactive barium sulfate with red phosphorus[15] and collecting the SO_2 formed in a 2 *N* NaOH solution. This solution of high specific activity was used to tag the sulfite for the exchange, an anhydrous sodium sulfite reagent. The high activity sulfite was stored in 2 *N* NaOH. In this medium no appreciable oxidation of sulfite takes place.

Procedure in the Exchange Experiments.—The reaction was carried out in water. Since the rate shows a dependence on the concentration of inert salts and on *p*H, care must be taken to control ionic strength and *p*H.

In order to avoid the oxidation of sulfite the reaction was carried out in an apparatus which permitted the withdrawal of samples in a nitrogen atmosphere. The nitrogen used was purified by bubbling it through a solution of a chromous salt.

The exchange was started by introducing into the reaction vessel a very small amount of radioactive sulfite of high specific activity, after the solution of reagents, inert salt and buffer had reached the desired temperature. The solution was then rapidly mixed by bubbling nitrogen and two 5-ml. samples were pipetted out to measure (i) the specific activity of sulfite at time zero, (ii) the concentration of sulfite by titration with *N*/100 iodine solution. To measure the variation of specific activity with time, five 5-ml. samples were pipetted out at suitable times. An additional sample was also taken to measure the *p*H. The exchange was then allowed to go to equilibrium in order to obtain the value of the specific activity at infinite time. A last sample was taken to measure again the concentration of sulfite, to check whether any oxidation of the sulfite had taken place during the reaction. In the event the concentration of sulfite had decreased more than 5% the run was disregarded.

Separation of the Reagents.—To stop the reaction the 5-ml. samples were poured into a proper volume of iodine solution (about *N*/10), so that the sulfite was rapidly oxidized to sulfate. Dilute iodine has virtually no action on alkylthiosulfates. Because of the high rate of exchange the concentrations of the reagents were kept low in order to have convenient reaction times. The quantity of reagents contained in 5 ml. was therefore insufficient to be handled for the specific radioactivity measurements. Hence, after oxidation with iodine, alkylthiosulfate carrier was added in known amount. Thereafter, sulfate was precipitated as the barium salt; this was centrifuged and the excess of barium ion precipitated as barium carbonate. After centrifugation the solution was made strongly acid with HCl and boiled. Under these conditions cleavage of the S–S bond took place with formation of mercaptan, which escaped, and of sulfate ion which was then precipitated as the barium salt for the specific activity measurement. In the experiments with the carboxymethyl derivative, hydrolysis caused the formation of thioglycolic acid which, unlike the other mercaptans, does not escape from the solution and may be easily oxidized. In this case it was found preferable to perform the hydrolysis in alkaline solution in the presence of an oxidant. Therefore in this case, after centrifugation of barium carbonate, sodium hydroxide and hydrogen peroxide were added and the solution boiled in order to complete oxidation. With this procedure both the sulfur atoms of the alkylthiosulfate were oxidized to sulfate and therefore the measured specific activity was one half of the specific activity of the external (SO_3) sulfur atom, *i.e.*, the one involved in the exchange.

Usually to evaluate the fraction of exchange only the activity of the alkylthiosulfate was measured, that is, the compound initially not radioactive. The measurement of

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(2) O. Foss, S. Furberg and H. Zachariasen, *Acta. Chem. Scand.*, **8**, 459 (1954).

(3) O. Foss and H. Zachariasen, *ibid.*, **8**, 473 (1954).

(4) J. A. Christensen and W. Drost-Hansen, *Nature*, **164**, 759 (1949).

(5) A. Fava, *Gazz. chim. ital.*, **83**, 88 (1953).

(6) F. Foerster and K. Center, *Z. anorg. allgem. Chem.*, **157**, 45 (1926).

(7) D. P. Ames and J. E. Willard, This Journal, **73**, 164 (1951).

(8) A. Fava and G. Pajaro, *Ann. Chim.*, **43**, 502 (1953).

(9) A. Fava and G. Pajaro, *ibid.*, **44**, 545 (1954).

(10) G. Pajaro and A. Fava, *Ric. Sci.*, **24**, 1903 (1954).

(11) A. Purgotti, *Gazz. chim. ital.*, **22**, 416 (1892).

(12) H. Bunte, *Ber.*, **7**, 1162 (1874).

(13) W. Spring, *ibid.*, **7**, 1162 (1874).

(14) W. Spring and E. Legros, *ibid.*, **15**, 946, 1938 (1882).

(15) R. E. Johnson and J. L. Huston, This Journal, **72**, 1841 (1950).

the activity of sulfite is rather troublesome and in routine work is better avoided. Nevertheless, a number of controlled experiments have been done measuring the activity of both reagents. In this case, since sulfite is always more or less accompanied by sulfate, the separation must be somewhat different. Sulfite was precipitated as the strontium salt by adding strontium nitrate. The precipitate was centrifuged and treated with HCl in an apparatus to collect the displaced SO_2. This was oxidized, sulfate was precipitated and its specific activity measured. This method is more involved and the results are affected by large errors, mainly due to the large exchange induced at time zero: about 30%, whereas the other method gives a zero-time exchange of about 5%.

Radioactivity Measurements.—The radioactivity was measured with a thin mica window Geiger–Mueller counter, connected to a scaling unit. To avoid correction for self-absorption, samples were mounted for counting in "thick layer"; reproducibility was better than 3%.

Results

Orders of Reaction.—According to the McKay equation the constant rate of exchange R is[16]

$$R = -\frac{1}{t}\frac{(S) \times (AT)}{(S) + (AT)} \ln (1 - F) \qquad (1)$$

and

$$R = 1(S)^n(AT)^m \qquad (2)$$

where k is the specific rate constant, n and m are the orders of reaction with respect to sulfite (S) and alkylthiosulfate (AT), respectively, F the fraction of exchange and t the time.

To determine R, $(1 - F)$ is plotted against time on semi-log paper. Straight lines are obtained whose slope is R. To evaluate n and m the concentration of sulfite and alkylthiosulfate was varied separately. Taking the logarithm of equation 2, n and m are obtained by the least squares method. The results, obtained using the carboxymethyl derivative, are summarized in Table I.

TABLE I

RATE OF EXCHANGE BETWEEN SODIUM SULFITE AND SODIUM CARBOXYLMETHYL THIOSULFATE

Temp., 25°; μ = 0.38 (NaCl added); pH 7.98

$(S) \times 10^3$	$(AT) \times 10^3$	$t_{1/2}$ sec. $\times 10^{-2}$	$R \times 10^7$, ^{1}mol. l.$^{-1}$ sec.$^{-1}$	$\frac{R \times 10^2}{(S) \times (AT)}$
5.0	2.0	76.2	1.3	1.3
5.0	10.0	38.2	6.0	1.2
5.0	15.0	26.1	10.0	1.3
5.0	20.0	17.4	15.8	1.6
5.0	5.0	54.6	3.2	1.3
2.3	5.0	86.4	1.3	1.1
11.2	5.0	38.4	6.2	1.1
15.8	5.0	23.4	11.2	1.4
20.8	5.0	19.8	14.0	1.3
			Av.	1.3

Orders of reaction result: n = 1.09 ±0.06 and m = 1.06 ±0.09.

Variation of Rate with Hydrogen Ion Concentration.—The rate of exchange is strongly affected by the hydrogen ion concentration. This effect may be studied in rather small range of pH because of the instability of alkylthiosulfates both at high and at low pH. Above pH 9 and below pH 3 the S–S bond is hydrolyzed and the measure of the fraction of exchange becomes difficult or even impossible. The results obtained between pH 8.4 and pH 4.1 are collected in Table II. Carboxymethyl thiosulfate was used.

TABLE II

INFLUENCE OF pH ON RATE OF EXCHANGE

Temp. 50°; μ = 0.38; (S) = (AT) = 5×10^{-3}

pH	8.4	8.0	7.2	6.2	5.8	5.3	4.1
$R \times 10^7$	11.1	10.3	9.6	4.0	2.1	0.90	0.17
$\frac{(HSO_3^-)}{(HSO_3^-)+(SO_3^{--})}$	0.01	0.03	0.14	0.65	0.82	0.93	.995

Heterogeneous Catalysis.—A set of experiments was run to test the homogeneity of the reaction, measuring the rate of exchange as a function of the surface/volume ratio of the reaction vessel. The variation of specific rate by varying this ratio by a factor of 100 is negligible and within the limits of the experimental error.

Influence of Inert Salts on Rate.—It was noticed that electrolytes act as positive catalysts. The effect of an increasing concentration of NaCl on rate of exchange between sulfite and sodium ethylthiosulfate is shown in Table III. The ethyl derivative was used in these experiments because of its high specific rate of exchange. It is thus possible to carry out the exchange at lower ionic strength still having convenient reaction times.

TABLE III

INFLUENCE OF NaCl ON RATE OF EXCHANGE

Temp. 25°; pH 7.4; (S) = (AT) = 3×10^{-3}

(Na^+)	0.034	0.055	0.072	0.100	0.140	0.177
μ	0.037	.058	.075	.103	.143	.180
$R \times 10^7$	4.13	5.25	5.92	6.93	8.18	8.97

It was also observed that the catalysis of electrolytes is particularly important when salts of polyvalent cations are present. In order to make clear this fact measurements were made of the specific rate of exchange that results when the ionic strength is kept at a constant value but is adjusted with different electrolytes. The results are summarized in Table IV. The exchange experiments were carried out at the ionic strength 0.1. Reagents and buffer contribute 0.051 unit of ionic strength; the rest is due to the salt listed in the top line.

TABLE IV

VARIATION OF RATE OF EXCHANGE AT CONSTANT IONIC STRENGTH VARYING THE TYPE OF ELECTROLYTE

Temp. 0°; pH 7.3; μ = 0.10; (S) = (AT) = 3×10^{-3}

Salt	KCl	K_2SO_4	$K_3Co(CN)_6$	$Pt(NH_3)_4Cl_2$	$Co(NH_3)_6Cl_3$
$R \times 10^7$	1.58	1.47	1.45	2.80	5.26

Structural Effects on Rate.—The temperature dependence of the rate of exchange was investigated for all the compounds listed at the beginning of this paper. Results are summarized in Table V. All experiments were carried at pH 7.3 using phosphate buffer; the ionic strength was 0.104. The concentration of the reagents was 3×10^{-3} eq./l. in the experiments with ethyl and allyl derivatives; 5×10^{-3} in all others. The temperature was controlled at the indicated values to ± 5/100 of a degree.

Application of the Arrhenius equation to the data in Table V permits the calculation of the frequency factors and the energies of activation.

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[16] A. C. Wahl and N. A. Bonner (editors), "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, 1951, p. 11.

TABLE V

TEMPERATURE DEPENDENCE OF THE RATE OF THE EXCHANGES SULFITE//ALKYLTHIOSULFATES

Ethyl thiosulfate

Temp., °C.	7.20	17.35	27.25	33.50	41.00
$k \times 10^2$, l. mole^{-1} sec.$^{-1}$	2.1	4.1	6.16	10.3	15.9

Benzyl thiosulfate

Temp., °C.	17.70	25.00	31.70	36.40	37.90	49.75
$k \times 10^2$, l. mole^{-1} sec.$^{-1}$	1.9	2.5	3.8	5.6	5.0	10.9

Allylthiosulfate

Temp., °C.	7.40	16.00	25.50	36.50
$k \times 10^2$, l. mole^{-1} sec.$^{-1}$	0.23	0.45	0.58	0.96

Ethane dithiosulfate

Temp., °C.	12.20	25.00	33.40	43.10
$^1/_2k \times 10^2$, l. mole^{-1} sec.$^{-1}$	1.4	2.9	4.2	6.8

Carboxymethyl thiosulfate

Temp., °C.	25.00	33.15	40.25	50.00
$k \times 10^2$, l. mole^{-1} sec.$^{-1}$	0.35	0.49	0.67	1.1

Least squares were used. The results of this analysis are given in Table VI. Free energies, entropies and heats of activation calculated according to the Eyring's rate theory are given in Table VII.

TABLE VI

ARRHENIUS FREQUENCY FACTORS AND ENERGIES OF ACTIVATION

Thiosulfate	$\log_{10} A$	E_a, kcal.
Ethyl	6.37 ± 0.20	10.33 ± 0.08
Benzyl	5.37 ± .28	9.65 ± .10
Allyl	3.94 ± .07	8.45 ± .03
Ethanedi	5.06 ± .21	9.02 ± .09
Carboxymethyl	4.34 ± .19	9.34 ± .08

TABLE VII

SPECIFIC RATE AT 25°, ENTROPIES, HEATS AND FREE ENERGIES OF ACTIVATION

Compound	$k \times 10^2$	$\Delta S\ddagger$	$\Delta H\ddagger$	$\Delta F\ddagger$
Thiosulfate	0.005	−32	13.8	23.3
$^1/_2$ Trithionate	0.035	−43	9.50	22.1
Ethylthiosulfate	5.9	−32	9.74	19.27
Benzylthiosulfate	2.0	−36	9.04	20.12
Allylthiosulfate	0.55	−43	7.86	20.53
$^1/_2$ Ethanedithiosulfate	2.8	−37	8.43	19.56
Carboxymethylthiosulfate	0.31	−41	8.73	21.23

Discussion

According to the above results the slow step involves the collision of a sulfite ion and an alkylthiosulfate one, the exchange being a bimolecular displacement of sulfite brought about by sulfite itself.

The catalysis by electrolytes demonstrates that the reaction involves ions of the same charge sign. An analysis of the data in Table III showed that the Brønsted equation is not followed. It is true, however, that the range of ionic strength in which this investigation was carried out is a little too high to expect the Debye–Hückel treatment to be strictly valid. However, also the treatment of Harty and Rollefson[17] which was proved valid in some cases for higher ionic strength, proved to be inapplicable. The specific effect of positive ions indicated by the results in Table IV could be accounted for by assuming that besides the reaction between free ions, also a reaction between ionic complexes, either of sulfite or alkylthiosulfate or perhaps of both, may occur. The existence of such complexes for sulfite has been shown by Ames and Willard.[18] For alkylthiosulfate the existence of such complexes seems not to have been investigated. In any case the intermediate seems to be preferentially associated with positive ions.

The fall in rate with lowering of pH is very interesting. It is obviously related to the well known experimental fact that whereas polythionates are rapidly desulfurated by sulfite ion in neutral and alkaline media according to the general equation

$$S_nO_6^{--} + SO_3^{--} \rightleftarrows S_{n-1}O_6^{--} + S_2O_3^{--}$$

in acid medium the equilibrium is displaced toward the left.

What makes the effect most interesting is the fact that for the sulfite–thiosulfate exchange, Ames and Willard[7] did not observe such an effect. In fact only a small (30%) decrease of the rate was observed from pH 12 to pH 5. The range of pH in which the fall in rate is observed corresponds to that in which sulfite ions are gradually converted to bisulfite.[19] An analysis of the data in Table II shows that the reaction of alkylthiosulfate with sulfite is about 100 times faster than the reaction with bisulfite. This figure is obtained from the consideration of the relative amounts of sulfite and bisulfite present at various pH's. The value of the dissociation constant[20] of bisulfite ion at 25° and zero ionic strength is $K = 6.2 \times 10^{-8}$. These experiments were made at 50° and at ionic strength 0.38 so that the value of the dissociation constant under these conditions was needed. Since the ionic strength is too high for calculating the activity coefficients by the D–H formula, and since there are no reported experimental values of them, the value of K was calculated from the variation of the dissociation constant for the bisulfate ion, for which enough data are reported,[21,22] on the assumption that the relative variation would be the same. The standard heat of formation[23] of sulfite and bisulfite ions was used to obtain the dissociation constant at 50°. The value obtained by these calculations is $K = 3.8 \times 10^{-7}$. With this value the relative amounts of sulfite and bisulfite present at various pH's were calculated and the fractions of bisulfite are listed in Table II.

If now R is the summation of two rates, one

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[17] W. E. Harty and G. K. Rollefson, THIS JOURNAL, **76**, 4811 (1954).

[18] D. P. Ames and J. E. Willard, *ibid.*, **75**, 3276 (1953).

[19] The possibility that alkylthiosulfate ions in the range of pH studied here are also converted into free acid, need not be considered: their basicity is in all probability of the same order of magnitude as that of the corresponding alkylsulfates, that is, extremely small in comparison with sulfite ion.

[20] H. V. Tartar and H. H. Garretson, THIS JOURNAL, **63**, 808 (1941).

[21] W. C. Bray and H. A. Liebhafsky, *ibid.*, **57**, 51 (1935).

[22] E. Eichler and S. Rabideau, *ibid.*, **77**, 5501 (1955).

[23] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamical Properties," 1952, U. S. Gov. Printing Office, Washington, D. C.

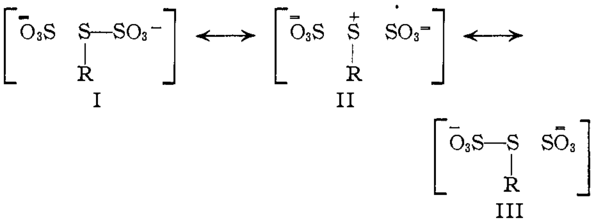
(R_1) characteristic of sulfite and the other (R_2) of bisulfite, we have

$$R = R_1(1 - x) + R_2x \qquad (3)$$

x being the fraction of bisulfite. Plotting R *versus* x one obtains a straight line whose intercepts at $x = 0$ and at $x = 1$ are R_1 and R_2, respectively. Graphically only the value of R_1, which is 11.2×10^{-7}, is obtained with some accuracy, whereas the value of R_2, because of its smallness, is better calculated from eq. 3 by introducing the known values of R, R_1 and x into it. In practice since R_1 is much larger than R_2, this calculation should be carried out only for the experiments at low pH where the contribution of $R_1(1 - x)$ to the total is small. Thus for the experiments at pH 6.2, 5.8, 5.3 and 4.1 the calculated values of R_2 are 0.123, 0.102, 0.124 and 0.115, respectively. The ratio R_1/R_2 is therefore about 100, which corresponds to a difference in free energy of activation of about 2.7 kcal.

The association of an hydrogen ion to a sulfite ion brings about a free energy decrease of about 9.5 kcal. Since the rate for the thiosulfate–sulfite exchange does not vary in going from sulfite to bisulfite, it may be deduced that the association of a H^+ to the intermediate also decreases its free energy by 9.5 kcal. On the other hand, in the alkylthiosulfate–sulfite complex the association of H^+ decreases the free energy by only $9.5 - 2.7 = 6.8$ kcal. This difference may be reasonably accounted for by the amount of charge carried by the two complexes: -4 and -3, respectively.

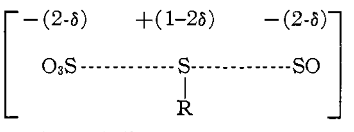
The question of which structure may be attributed to the intermediate complexes arises. In analogy with the bimolecular nucleophilic substitution at the carbon atom, the hypothesis can be made that the intermediate (for instance in the alkylthiosulfate–sulfite reaction) is a resonance hybrid of the structures



$$\left[\bar{O}_3S\quad \underset{R}{\underset{|}{S}}—SO_3^-\right] \longleftrightarrow \left[\bar{O}_3S\quad \underset{R}{\underset{|}{\overset{+}{S}}}\quad SO_3^=\right] \longleftrightarrow \left[\bar{O}_3S—\underset{R}{\underset{|}{S}}\quad \bar{S}O_3\right]$$

I II III

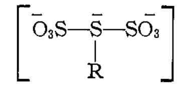
The hybrid can be represented by



$$\left[\overset{-(2\text{-}\delta)}{O_3S}\cdots\cdots\underset{R}{\underset{|}{\overset{+(1-2\delta)}{S}}}\cdots\cdots\overset{-(2\text{-}\delta)}{SO}\right] \quad \text{IV}$$

where the dotted lines represent partial covalent bonds. The actual distribution of charge in the intermediate (*i.e.*, the value of δ) is difficult to predict. However, it may be stated that since the sulfur atom of the SO_3 groups is more electronegative than the central sulfur atom, *the latter is in the intermediate less negative than it is in the initial state.* Analogous structures can be written for the thiosulfate–sulfite and trithionate–sulfite complexes.

The structures of the type IV assumed above involve only s and p orbitals of the central sulfur. For sulfur, however, 3d orbitals are available and there exists the possibility that in the intermediate one d orbital may be used. If this were the case the resulting structure for the alkylthiosulfate–sulfite complex would be



$$\left[\bar{O}_3S—\underset{R}{\underset{|}{\bar{S}}}—\bar{S}O_3\right] \quad \text{V}$$

Here the central sulfur has 10 electrons, one electron pair having been promoted into a 3d orbital. The configuration of the central sulfur would probably be sdp^3 trigonal bipiramidal, with vertices occupied by the entering and the leaving group. In this type of structure the distribution of charge *is such that the central sulfur is more negatively charged than in the corresponding initial state.*

The question of how large may be the relative contribution of structures of type IV and V to the structure of the intermediates cannot be easily solved for the experimental results obtained in the present work do not allow a definite assignment. Nevertheless, there are some facts that may be interpreted as pointing to the type IV structures as more probable. The absence of a pH effect in the thiosulfate–sulfite exchange is one of these. In fact, if the decrease of free energy for the association of H^+ to a sulfite ion and to the thiosulfate–sulfite complex is about the same, it may be deduced that in the latter the charge on the SO_3 groups is nearly the same as on the sulfite ion. This requirement is more closely fulfilled if the structure of the intermediate is of type IV (VI) rather than V (VII).

$$\underset{\text{VI}}{\left[\overset{-(2-\delta)}{O_3S}\cdots\cdots\overset{-2\delta}{S}\cdots\cdots\overset{-(2\text{-}\delta)}{SO_3}\right]} \qquad \underset{\text{VII}}{\left[\bar{O}_3S\text{-}\bar{S}\text{-}\bar{S}O_3\right]}$$

Let us consider the data in Table VII. The compounds listed here may be divided in two groups: in one the alkylthiosulfates, in the other the compounds: thiosulfate, trithionate and one of the alkylthiosulfates, for instance the ethyl derivative. The compounds in this second group differ from one another by the substituent at the divalent sulfur atom, that is, at the reaction center. It is difficult, comparing the rates for these three compounds, to draw any conclusions about the relative importance of structures of type IV and V in the intermediate, since too many factors (electronic, steric and total charge) concur to determine the stability of the intermediate. Rather, the fact that the free energy decreases in the order: thiosulfate, trithionate, alkylthiosulfate suggests that the total charge and the possibilities of distributing it are the predominant factors. Let us now compare the rate for the alkylthiosulfates. These compounds differ from one another by the substituent in β. In all cases a $-CH_2-$ group being between the substituent and the reaction center, one might expect that only steric and inductive effects are present. Looking through the figures given in Table VII we observe that, although the rate does not vary much from one compound to another, varying only by a factor of 20 in the limiting cases, these comparatively small variations of rate arise from the mutual compensation of quite large variations of the energy and entropy terms. That entropy and heat of activation tend to compensate each other yielding a minimum of free energy change, is quite a general phenomenon. However, it will be noted in these examples that the direction of the rate change is determined by the entropy rather than the heat change, whereas most commonly it is the other way around. The phenomenon is not exceptional, however, and several examples of such a behavior are reported in literature.[24,25] The present case seems to fit with the observation that for the nucleophilic reactions at the carbon atom the β-substitution in the substrate causes large variations both in the entropy and in the heat change. This has been interpreted as a steric effect,[26] and it may be so also in the present case.

However, the comparison of the allyl and ethyl systems, for which a tenfold variation of the rate is observed, deserves a more thorough discussion. In the allyl compound there is a vinyl group in the β-position whereas, in the ethyl compound, there is a methyl group. As far as inductive electronic effects are concerned the vinyl group is known to be electron attracting while the methyl group is known to be electron releasing. If the structure of the intermediate is IV it may be expected that the introduction of an electron attracting group destabilizes the complex, and *vice versa* if the structure is V. Therefore, neglecting for a moment the steric effect, it could be concluded that structure IV is the more nearly correct. Let us see now how big a contribution of steric effect there might be in this particular example. The substitution of a methyl group by a vinyl one should roughly correspond to the substitution of a methyl by an ethyl group. Taking for comparison the nucleophilic reactions at the carbon atom, the difference in rate, due to steric effect, should correspond to the difference between n-propyl and n-butyl derivatives. At least for halogen substitution this difference is very small and negligible, although it may become larger when incoming and outgoing groups are as large as the SO_3 groups. Yet it seems hard to attribute the entire decrease in rate to steric effect only, but it appears more reasonable to attribute it to steric plus electronic inductive effects acting in the same direction, and conclude that structure V contributes little to the intermediate, the latter being more correctly represented by the hybrid IV. We think, however, that the study of other systems, for which the steric effect is more clearly separable from the electronic one, is highly advisable. Such systems are for instance the p-substituted benzyl thiosulfates (such as p-NO_2 and p-OCH_3) for which the steric effect could be considered constant and the variations in rate could be attributed to electronic effects only.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Vapor Phase Photolysis of 2-Methylbutanal at Wave Length 3130 Å.[1]

BY JERRY T. GRUVER AND JACK G. CALVERT

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Vapor phase photolyses of 2-methylbutanal are made in 3130 Å. and full mercury arc light. CO, H_2, CH_4, C_2H_4, C_3H_6, 1- and 2-C_4H_8, n-C_4H_{10} and 3,4-dimethylhexane are the products identified. The quantum yields or rates of the products are determined in experiments at various temperatures, concentrations and intensities. The data suggest the importance of two primary processes: $C_2H_5CH(CH_3)CHO + h\nu \rightarrow C_2H_5CHCH_3 + CHO$ and $C_2H_5CH(CH_3)CHO + h\nu \rightarrow C_2H_4 + C_2H_5CHO$. Activation energies and pre-exponential factors for the decomposition, H-abstraction, disproportionation and combination reactions of the *sec*-butyl radical are derived from the data.

The photolysis of 2-methylbutanal was investigated to determine its value as a source of *sec*-butyl radicals, and to establish the effect of 2-methyl substitution on the efficiency of the ethylene forming primary process of n-butyraldehyde photolysis.

Experimental

Apparatus.—The all-glass photolysis system consisted of a quartz photolysis cell (50 mm. long, 30 mm. diam.), a glass circulating pump and a trap. This system was isolated from stopcocks by mercury valves. The cell was suspended in an aluminum block furnace (regulated to ±1°). Radiation from a Hanovia type A (S-500) burner, operated on a regulated 3 amp. a.c. current, was filtered to isolate wave length 3130 Å.[2] The light beam was collimated by a series of lenses and stops so that a fairly homogeneous beam of radiation filled the cell volume (35.3 cc.) almost completely. The geometric arrangement of all components in the light train remained fixed during the study at 3130 Å. The incident intensity was lowered in some runs with uniform density filters. A photomultiplier–amplifier system was used to measure the fractions of light absorbed. Absolute intensities were estimated by acetone vapor photolysis (at temperatures near 110°) at spaced intervals during the course of the photochemical runs. In one series of runs the filter system was removed, the arc moved near to the cell, and a single lens was used for collimation. In these experiments the full radiation of the mercury arc was incident on the cell, and the absorbed intensity ($2500 < \lambda < 3200$ Å.) was estimated by acetone photolysis to be about 90 times the maximum intensity used in the 3130 Å. experiments.

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