cessful. This suggests that K_f, as defined in (7), is also a small number.

The assumption that the total vanadium(V) concentration is being measured analytically is plausible. This is particularly true in instances where large excesses of glycerol were employed; under these circumstances the V(V) concentration was obtained by difference, the V(IV) concentration actually being measured. That data obtained through the direct measurement of V(V) can be correlated to these tends to support the original assumption.

According to (8) the experimentally evaluated rate constant k'' is equal to the product of the three constants appearing in the numerator; it is thus dependent upon the equilibrium constant for the formation of the coördination complex. Of the three substances oxidized, it is reasonable to expect that the glycerol molecule, with relatively unhindered hydroxyl groups and effectively doubled sites for reaction, would enter into an equilibrium most favorable for complex formation, followed by *cis*-1,2-cyclohexanediol and then the *trans*-isomer. This order is in agreement with experimental fact; if the magnitude of the pseudo second-order rate constants for the oxidation of these substances is compared for the same set of reaction conditions, it is seen that they stand in a ratio of approximately 4:2:0.8, respectively.

While the numerical value of the Arrhenius activation energy is somewhat uncertain as measured, the magnitude is probably correctly indicated. The rate-determining step in the process thus does not appear to involve the direct cleavage of a carbon–carbon bond. The intermediate formation of some entity appears to reduce considerably the energy requirements for this process.

STANFORD, CALIF.

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

Kinetics of Oxidation by Aqueous Polysulfide Solutions. II. Rate Dependence of the Oxidation of *m*-Toluic Acid on the Concentration and Chain Length of the Polysulfide Oxidant[1]

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The rate of oxidation of sodium *m*-toluate by aqueous sodium polysulfide solutions is proportional to the square root of the concentration of polysulfide molecules. This is true when the correlation is made at a constant value of *n*, the average chain length[1b] in $S_{n+1}^{=}$, over the range of values of *n* from 1.3 to 4.0. The correlation must be made at a constant value of *n* since the rate also depends approximately linearly on *n*. The concentrations of polysulfide used are corrected for sulfur disproportionation reactions which occur at reaction temperature and for the percentage of sulfide in the vapor as H_2S. Polysulfide is the only oxidant although several other sulfur species are present. Neither sodium thiosulfate nor sodium sulfate alone oxidizes sodium *m*-toluate, and sulfite and polythionate are believed not to be present. The kinetic data extrapolate to give zero rate of oxidation at zero concentration of polysulfide. The mechanism most consistent with these and earlier data[2] involves reversible fission of a polysulfide molecule to give two polysulfenyl radicals which then abstract a benzyl hydrogen in a slow step which has a rate constant proportional to the over-all rate of oxidation (equations 14, 15 and 16). The dependence on *n* arises from the fact that S–S bonds over the range $S_{2.3}^{=}$–$S_{5.0}^{=}$ are of similar energy and the rate of reaction 14 depends on the total number of S–S bonds.

Introduction

Aqueous solutions of sodium polysulfide quantitatively oxidize sodium *m*-toluate to sodium isophthalate at 250–350°. Part I of this series[2] presented evidence on the mechanism of this reaction which the present paper extends. It was shown that with polysulfide oxidant present in excess, the reaction rate is first order in *m*-toluic acid concentration. A mechanism which predicts the kinetic dependence to be first order in *m*-toluic acid and 0.5 order in polysulfide was presented. While the first work suggested that the order in polysulfide was 0.5, further work was necessary to substantiate this. Data now are presented which show that the dependence on the actual concentration of sodium polysulfide in solution at reaction temperature is 0.5 over the range of polysulfide chain lengths[1b] accessible in this study, $S_{2.5}^{=}$ to $S_5^{=}$. Since the rate is found to be dependent on chain length as well as concentration of polysulfide, one of these must be held constant while correlating the rate of oxidation with the other.

Experimental

Analysis.—The analytical techniques which use *m*-toluic acid-C^{14} and paper chromatography have been described.[2] The constant volume micro reactor also has been described.[3]

The most satisfactory analysis for sulfide, polysulfide-sulfur, sulfite, thiosulfate and sulfate together was taken from analyses conveniently summarized in the recent book by Kolthoff, Belcher, Stenger and Matsuyana.[4] The method chosen was found to be the most accurate on known solutions. It involves determining the number of sulfur atoms *n* in each polysulfide molecule $S_{n+1}^{=}$ using the procedure of Schulek.[2,4a,5,6] This polysulfide-sulfur, expressed in g. atoms/l., is symbolized (S^0) in the discussion below. Sulfide is precipitated with freshly prepared zinc carbonate; the zinc sulfide is filtered, redissolved in acidified iodine, and titrated with thiosulfate.[4b] An aliquot of the filtrate is

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[1] (a) Work supported by Oronite Chemical Company. Presented at the American Chemical Society Meeting, September 1959, Atlantic City, New Jersey. (b) Chain length refers to the number of sulfur atoms in the average polysulfide molecule, not to a kinetic chain length.

[2] W. A. Pryor, THIS JOURNAL, **80**, 6481 (1958).

[3] W. A. Pryor, V. C. Davis and M. Ausman, *Ind. Eng. Chem.*, **51**, 129 (1959).

[4] I. M. Kolthoff, R. Belcher, V. A. Stenger and G. Matsuyana, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957: (a) pp. 292, 307, (b) pp. 295, 300, (c) p. 299 and references given there.

[5] E. Schulek and E. Koros, *Acta Chim. Acad. Sci. Hung.*, **3**, 111 (1953).

[6] E. Schulek, *Z. anal. Chem.*, **65**, 352 (1925).

added to excess acidified iodine and back-titrated with thiosulfate to determine the sum of sulfite plus thiosulfate.[4b] Formaldehyde is added to a second aliquot of the filtrate to remove sulfite and thiosulfate is determined alone.[4b] In the work reported here, sulfite is not present in measurable amounts. Although this procedure would lead to polythionates being calculated as thiosulfate, it is extremely doubtful that polythionates exist in this sulfide-rich,[4b] basic solution,[7,8] after equilibration at 288°. Sulfate is determined as barium sulfate.[2] Material balance in sulfur indicates these are the only sulfur species present in measurable concentration.

Typical Experiment (Table III).—Two ml. of a sodium polysulfide solution which is 1.0 *M* in sodium trisulfide, 0.10 *M* in sodium thiosulfate and 0.006 *M* in sodium sulfate, and with *p*H 12.10, is added to the microbomb[3] along with 2.00 ml. of water, 10.00 mg. of radioactive *m*-toluic acid and 37.5 mg. of purified[2] sulfur. The reaction mixture is heated and shaken for 40 minutes at 288°. The bomb is opened, a paper chromatogram prepared and counted in the liquid scintillation counter. It showed 44.8% *m*-toluic and 54.6% isophthalic acid, giving a rate constant of 3.34×10^{-4} sec.$^{-1}$. Table I gives the analysis of the oxidant before and after reaction. The sulfur recovered from the bomb is in excellent agreement with that added and good oxidation–reduction balance also is found: disproportionation reactions consume 0.22 *M* polysulfide-sulfur and produce 0.15 *M* sulfide, 0.03 *M* thiosulfate and 0.04 *M* sulfate. Identical kinetic runs, but held for 20, 30 and 40 minutes at 288°, gave the same analysis for sulfur species ± 5% and rate constants for oxidation of 3.17, 3.32 and 3.34×10^{-4} sec.$^{-1}$, respectively.

The rate of cooling the bomb is without measurable effect on the concentration of sulfur species. Either the position of equilibrium is affected very slightly by changes in temperature, or the redistribution of sulfur species is very fast at elevated temperatures, or both.

The presence or absence of oxygen is without measurable effect.

TABLE I

DISPROPORTIONATION OF POLYSULFIDE OXIDANT AT 288°[a]

Molarity	Before reacn.	After reacn.
($S^=$)	0.50	0.65
(S^0) as polysulfide	1.00	1.08
sulfur, elemental	1.30	0
($S_2O_3^=$)	0.05	0.08
($SO_4^=$)	0.003	0.04
Total S[b]	1.90	1.93

[a] The symbol (S^0) is defined in the text. [b] Includes twice ($S_2O_3^=$) since it is 2 normal in sulfur.

Molarity of Polysulfide at 288°.—The following procedure was used to calculate the molarity of polysulfide of average length $n+1$ in solution at reaction temperature, ($S_{n+1}^=$). The total sulfide and polysulfide-sulfur are titrated as described and the H_2S pressure at 288° is measured. The sulfide present as H_2S is subtracted from the total sulfide to give sulfide in solution, ($S^=$). (This correction is small except for 0.6 and 0.3 *M* sulfide where about 40% of the sulfide is in the vapor.) Since there is no colloidal sulfur present and all elemental sulfur is attached to a sulfide molecule, the molarity of polysulfide is equal to the molarity of sulfide. That is, this equation goes to completion

$$nS^0 + S^= \longrightarrow S_{n+1}^=$$

Therefore, at any time the total concentration of polysulfide is identical to the titrated concentration of sulfide. The average *n* is the ratio of polysulfide-sulfur to sulfide: $n = (S^0)/(S^=)$. This *n* represents an average chain length for the species $S^=$, $S_2^=$, $S_3^=$, . . . $S_x^=$, $S_{x+1}^=$, $S_{x+2}^=$, etc. The distribution of chain lengths about the average was not measured, but it is shown below that changes in distribution do not affect any of the conclusions reached. There is also a distribution of sulfide species as H_2S_x, HS_x^- and $S_x^=$, the most probable undoubtedly being HS_x^-. No attempt to distinguish these was made and the symbol $S_x^=$ represents the sum of all such species in solution.

The total volume of all runs was 4.00 ml. at 25°, or 5.3 ml. at 288°. Molarities quoted are at 25° but the relative rates are not affected by correcting for volume expansion.

Data

Table II gives data for the oxidation of *m*-toluic acid from a total of 88 bomb runs. The table shows the number of points determined in each kinetic run, the concentration of sulfide, polysulfide-sulfur, thiosulfate and sulfate after equilibrium at 288°, and the rate constant. Each code letter includes a range of conversions of *m*-toluic to isophthalic acid and both the analyses for sulfur species and the rate constant are independent of conversion. Table II, in addition to giving the concentration of sulfide, also gives the average value of *n* in $S_{n+1}^=$. The table includes four concentrations of polysulfide, each over a range of values in *n*. Note that the rate increases both with the concentration of $S_{n+1}^=$ and with the value of *n*. Therefore, in correlating the rate of oxidation of *m*-toluic acid with the *concentration of* $S_{n+1}^=$, it is important to make comparisons at constant *n*.

TABLE II

THE RATE OF OXIDATION OF *m*-TOLUIC ACID BY VARIOUS SODIUM POLYSULFIDE SOLUTIONS

No. of runs	Av. molarity after equilibration at 288° $S^=$	S^0	$S_2O_3^=$	$SO_4^=$	Av. *n* in ($S_{n+1}^=$)	$k \times 10^4$ (sec.$^{-1}$)
7	2.3	4.0	0.63	0.04	1.7	7.3
3	2.3	4.3	.55	..	1.9	7.3
4	2.3	4.7	.62	..	2.0	8.4
5	2.3	5.5	.42	..	2.4	9.2
8	1.3	2.0	.31	0.05	1.5	3.8
3	1.3	2.0	.38	..	1.5	5.0
4	1.3	2.6	.30	..	2.1	5.4
5	1.3	2.8	.32	..	2.3	6.8
3	1.3	3.4	.38	..	3.0	8.1
13	0.60	0.9	.15	0.07	1.5	2.6
3	.60	0.9	.20	..	1.5	2.6
3	.60	1.2	.12	..	2.0	3.2
3	.60	1.6	.08	..	2.7	4.5
2	.60	2.4	.07	..	4.0	6.7
11	.30	0.4	..	..	1.3	1.69
3	.30	0.4	..	..	1.3	1.87
4	.30	0.8	..	..	2.7	3.16
4	.30	1.1	..	..	3.7	4.2

Figure 1 is a graph of the rate constant *k versus* the average chain length $n + 1$ in $S_{n+1}^=$. Four straight lines through these points are shown, one for each concentration of polysulfide. The lines are fit to the data by least squares and the standard deviation is 2.5% in the worst case. These lines show the effect of increasing the average chain length at constant concentration of total polysulfide. The lines all show zero rate of oxidation for $n = 1$, *i.e.*, pure sulfide, as theory demands.

The lines in Fig. 1 were used to interpolate the rate of oxidation to desired values of *n* in order to correlate the rate of oxidation with the concentration of $S_{n+1}^=$ at constant *n*. Figure 2 shows this interpolated rate from Fig. 1 *versus* the square root of the concentration of polysulfide for $n = 1$, 2 and 3. In each case, a straight line is obtained showing the rate is proportional to the square root of the concentration of polysulfide regardless of the average chain length of the polysulfide. Note that

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(7) A. Fava and D. Dino, *Gazz. chim. ital.*, **83**, 98 (1953); *C. A.*, **47**, 11914e (1953).

(8) A. M. Kognavoskii, T. M. Rovinskaya and P. N. Taran, *Ukrain. Khim. Zhur.*, **23**, 257 (1957); *C. A.*, **51**, 12718f (1957).

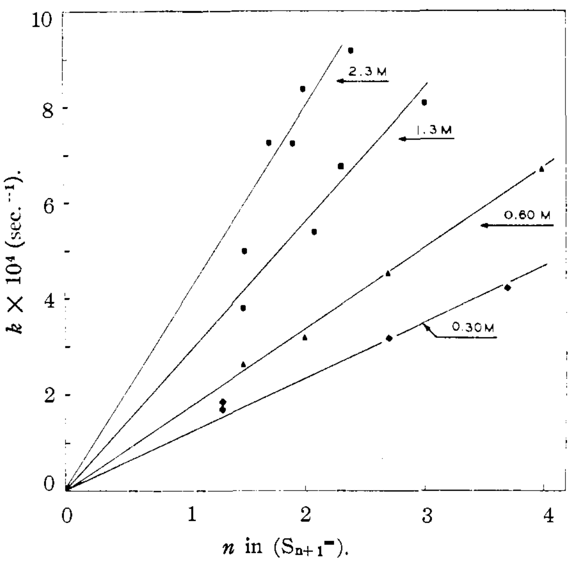


Fig. 1.—The rate constant for oxidation *vs.* the average chain length of the polysulfide oxidant.

since the lines all extrapolate to zero rate of oxidation at zero concentration of polysulfide, oxidation by other species is minor.

Figure 3 has the same data as shown in Fig. 1, but on a log–log graph. A least squares treatment of these data shows that within experimental error all four lines have the same slope, namely, 0.88. Since n is the number of S–S bonds in the polysulfide, this implies that the rate of oxidation is almost proportional to the number of such bonds in the average polysulfide molecule present.

One further conclusion can be drawn from the fact that all four lines in Fig. 3 have the same slope; as long as this is true, all values of n will give the same order of the oxidation in $S_{n+1}^{=}$. If the order in polysulfide is independent of chain length it is, of course, also independent of the distribution of chain lengths around the average. That is, even if the distribution $S^{=}$, $S_2^{=}$, . . . $S_x^{=}$, $S_{x+1}^{=}$, etc., changes with the total concentration of the polysulfide species, the kinetic order remains 0.5 in the average species since it is 0.5 in each of the individual species except $S^{=}$.

Discussion

The mechanism for this oxidation has been tentatively suggested[2] to be oxidation by polysulfide through free radical intermediates. Before examining the present data further, the basis for these previous conclusions must be reviewed.

Polysulfide Is the Active Oxidant.—Polysulfide is believed to be the active oxidant both because other sulfur species which are present can be shown not to be oxidants and because the kinetic data can be explained readily if polysulfide is the oxidant.

The sulfur species definitely present in these solutions are: sulfide, polysulfide-sulfur, thiosulfate and sulfate. It is unlikely that colloidal sulfur is present for many reasons: the oxidation rate is unaffected by shaking, the reaction solution at temperature is clear, the oxidant is homogeneous both before and after reaction and colloidal sulfur is unstable in basic and or sulfide-rich solutions even at moderate temperatures.[9–12] Measurable concentrations of sulfite are not present in these solutions. It is known that sulfite is converted to thiosulfate by polysulfide or by sulfur.[13] Polythionates and sulfite also react, eventually leading to thiosulfate as the sole product,[14] and sulfide converts polythionates to thiosulfate.[4c]

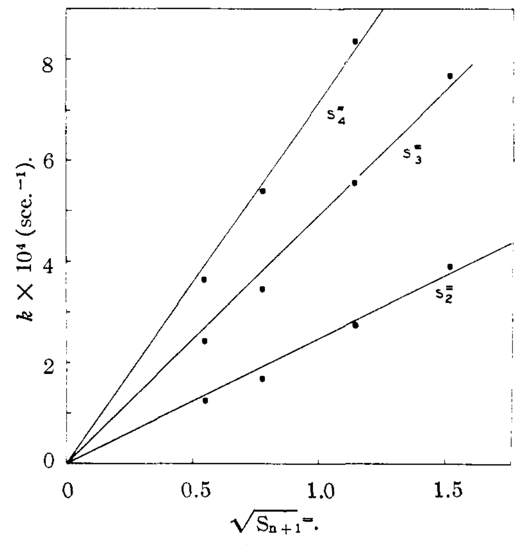


Fig. 2.—The rate constant for oxidation *vs.* the square root of the concentration of polysulfide.

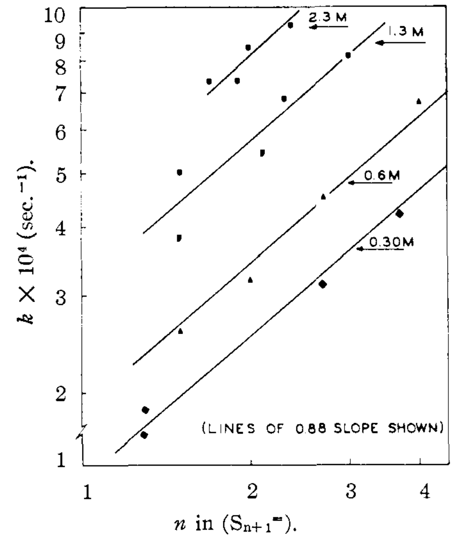


Fig. 3.—The rate constant for oxidation *vs.* the average chain length of the polysulfide oxidant.

Of the species present, sulfide cannot be an oxidant since it is the lowest valence state of sulfur. Sulfate is stable in the solutions and alone does not oxidize m-toluic acid (runs 374, 394, Table III).

[9] H. Gerischer, *Z. anorg. allgem. Chem.*, **259**, 220 (1949).

[10] D. Peschanski, *Compt. rend.*, **227**, 770 (1948).

[11] F. Caujolle, D. Meynier and P. Payssot, *Ann. inst. hydrol. et climatol.*, **23**, 73 (1952); *C. A.*, **47**, 5834c (1953).

[12] P. D. Bartlett, G. Lohaus and C. D. Weis, THIS JOURNAL, **80**, 5064 (1958).

[13] M. Schmidt and H. Heinrich, *Angew. chem.*, **70**, 572 (1958); A. Kurtenacker and R. Wollak, *Z. anorg. allgem. Chem.*, **161**, 201 (1927); E. Schulek and E. Koros, *Acta Chem. Acad. Sci. Hung.*, **3**, 125 (1953); O. Foss, *Acta Chem. Scand.*, **4**, 404 (1950).

[14] A. Kurtenacker, *Z. anorg. allgem. Chem.*, **134**, 265 (1924).

TABLE III

SODIUM SULFATE AND THIOSULFATE OXIDATION RUNS. SALT EFFECT ON RATE

Run no.	Min. at 288°	Molarity added[b]						Molarity recovered				% S re-covd.	% Recovd.		% Radio-activity recovd.	$k \times 10^4$ (sec.$^{-1}$)
		S^0[a]	Na_2SO_4	$Na_2S_2O_3$	NaOH	NaCl	*m*-Toluic acid	S^0[a]	$S^=$	$S_2O_3^=$	$SO_4^=$		*m*-Toluic	IP[a]		
374	120	0	1.00	0	0	0	0.0180	..	..	..	..	..	98.3	1.2	75	0.01
394	120	0	1.00	0	0.025	0	.092	..	..	..	..	..	97.6	0.9	106	0
396	5	0	0	1.0	.050	0	.0182	0.16	0	0.90	0.17	106	99.4	0.36	103	0
397	5	0	0	1.0	.125	0	.0180	.11	0	1.07	.07	115	99.9	0.04	96	0
415	120	0	0	1.0	.050	0	.0094	.04	0	1.07	.09	113	95.8	1.3	107	0.01
73[c,d]	..	0.73	0	0	.50	0	....[c]	..	..	..	..	..	..	..	..	1.19 ± 0.06
365[d]	120	0.73	0	0	.50	0.50	.0178	..	..	..	..	..	68.3	29.2	101	1.24
530[d]	120	0.73	0	0	.50	1.00	.00608	..	..	..	..	..	69.3	30.7	87	1.00

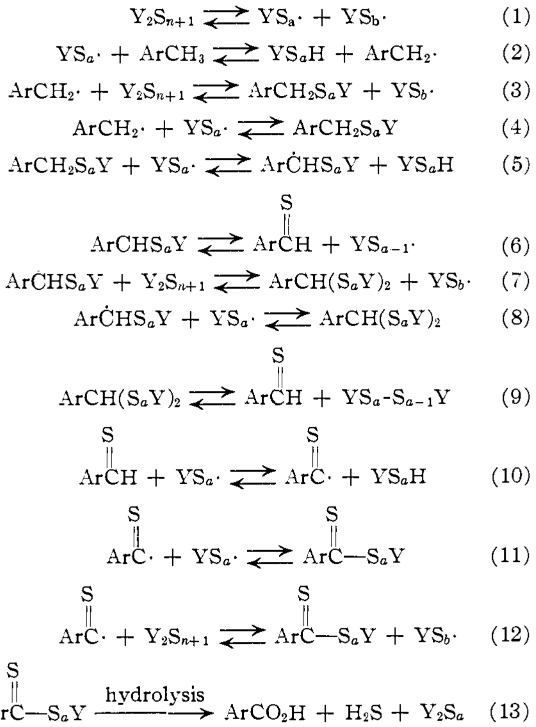
[a] IP = isophthalic acid, S^0 = polysulfide sulfur (see Experimental). [b] 4.00 ml. total reaction volume at 25°. [c] Runs 73, 38, 37 and 106 from Table III, ref. 2. [d] Oxidant is 0.73 *M* S^0 + 0.50 *M* NaOH (see ref. 2).

Thiosulfate is sufficiently stable in basic solutions at these temperatures so that alone it does not oxidize *m*-toluic acid at an appreciable rate (runs 396, 397, 415 Table III).

Several lines of evidence favor the polysulfide molecule as the oxidant: it is known to cleave to free radicals above 180°,[15] the related radical is known to be capable of abstracting hydrogen[16] and the kinetics are satisfied by this species. As seen below, not only can the rate of oxidation be correlated with the concentration of polysulfide but the kinetics show polysulfide to be the only oxidant of importance.

This Reaction Involves Free Radicals.—Support for the free radical nature of the oxidation can be found in the fact that basic aqueous solutions of polysulfide give blue colors above about 130°.[17] In several cases paramagnetic resonance spectra show free radicals to be present when sulfur species are observed to be colored.[18]

Mechanism.—Assuming the reaction is a radical oxidation by polysulfide, the complete mechanism for oxidation of arylmethyl compounds to carboxylic acids will include the steps



$$Y_2S_{n+1} \rightleftharpoons YS_a\cdot + YS_b\cdot \qquad (1)$$

$$YS_a\cdot + ArCH_3 \rightleftharpoons YS_aH + ArCH_2\cdot \qquad (2)$$

$$ArCH_2\cdot + Y_2S_{n+1} \rightleftharpoons ArCH_2S_aY + YS_b\cdot \qquad (3)$$

$$ArCH_2\cdot + YS_a\cdot \rightleftharpoons ArCH_2S_aY \qquad (4)$$

$$ArCH_2S_aY + YS_a\cdot \rightleftharpoons Ar\dot{C}HS_aY + YS_aH \qquad (5)$$

$$ArCHS_aY \rightleftharpoons Ar\overset{\overset{\mathrm{S}}{\|}}{C}H + YS_{a-1}\cdot \qquad (6)$$

$$Ar\dot{C}HS_aY + Y_2S_{n+1} \rightleftharpoons ArCH(S_aY)_2 + YS_b\cdot \qquad (7)$$

$$Ar\dot{C}HS_aY + YS_a\cdot \rightleftharpoons ArCH(S_aY)_2 \qquad (8)$$

$$ArCH(S_aY)_2 \rightleftharpoons Ar\overset{\overset{\mathrm{S}}{\|}}{C}H + YS_a\text{-}S_{a-1}Y \qquad (9)$$

$$Ar\overset{\overset{\mathrm{S}}{\|}}{C}H + YS_a\cdot \rightleftharpoons Ar\overset{\overset{\mathrm{S}}{\|}}{C}\cdot + YS_aH \qquad (10)$$

$$Ar\overset{\overset{\mathrm{S}}{\|}}{C}\cdot + YS_a\cdot \rightleftharpoons Ar\overset{\overset{\mathrm{S}}{\|}}{C}\text{—}S_aY \qquad (11)$$

$$Ar\overset{\overset{\mathrm{S}}{\|}}{C}\cdot + Y_2S_{n+1} \rightleftharpoons Ar\overset{\overset{\mathrm{S}}{\|}}{C}\text{—}S_aY + YS_b\cdot \qquad (12)$$

$$Ar\overset{\overset{\mathrm{S}}{\|}}{C}\text{—}S_aY \xrightarrow{\text{hydrolysis}} ArCO_2H + H_2S + Y_2S_a \qquad (13)$$

where the last, irreversible hydrolysis step drives the reaction to completion. In these equations: $n + 1 = a + b$, $1 < a \sim b < 5$, Y can be H, Na, $ArCH_2$, ArCS, etc., and all sulfide radicals are considered to be identical in their ability to abstract hydrogen. Equation 1 is reversible fission to two polysulfenyl radicals. Equation 2 is benzyl hydrogen abstraction. Although this reaction is known to be reversible,[16] in this system the reverse reaction must be slow (see below). Equations 3 through 12 represent further oxidation, always by hydrogen abstraction by a polysulfenyl radical. The resulting organic radical can stabilize by either combining with a polysulfenyl radical (equations 4, 8, 11), by displacement on an S–S bond (equations 3, 7, 12) or by *β*-fission (equation 6).

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(15) S. F. Birch, T. V. Cullum and R. A. Dean, *J. Inst. Petroleum*, **39**, 206 (1953); R. J. Kern, THIS JOURNAL, **77**, 1382 (1955); T. Otsu, *J. Polymer Sci.*, **21**, 559 (1956); E. R. Bertozzi, F. O. Davis and E. M. Fettes, *ibid.*, **19**, 17 (1956); H. C. Cutforth and P. W. Selwood, THIS JOURNAL, **70**, 278 (1948); T. E. Ferington and A. V. Tobolsky, *ibid.*, **77**, 4510 (1955); M. Nakasaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 403, 518 (1953).

(16) For references see: C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 322–326. Also see C. Walling and R. Rabinowitz, THIS JOURNAL, **81**, 1137 (1959).

(17) G. N. Lewis, M. Randall and F. R. v. Bichowsky, *ibid.*, **40**, 356 (1918).

(18) For example, sulfur is blue in liquid ammonia,[17] S_2 (solid) is purple (presumably a triplet state),[19] S_8 (solid) is green (presumably a linear diradical),[20] sulfur in certain salt eutectics at 200–400° gives blue solutions which are paramagnetic,[21] sulfur gives solutions which vary from yellow to blue and are paramagnetic in oleum,[22,23] and finally an ammonium polysulfide oxidant similar to the sodium polysulfide oxidant used here is blue at temperatures of about 300° when observed in glass ampules. Observing blue color is not sufficient evidence to establish the presence of free radicals, and instances are known where colors are observed in cases that clearly do not involve radicals.[24a] When $S_2O_3^=$ is displaced from sulfenyl thiosulfate, $RS\text{–}S_2O_3^-$, by OH^-, blue color is observed, and this reaction is undoubtedly ionic.[24b] Also, the sodium and potassium salts of 1-anthraquinone-sulfenic acid are colored,[25a] but are apparently anomalous in this respect.[25b]

(19) F. O. Rice and C. Sparrow, THIS JOURNAL, **75**, 848 (1953).

(20) F. O. Rice and J. Ditter, *ibid.*, **75**, 6066 (1953).

(21) J. Greenberg and B. R. Sundheim, *J. Chem. Phys.*, **29**, 461 (1958).

(22) D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **78**, 6411 (1956).

(23) D. J. E. Ingram and M. C. R. Symons, *J. Chem. Soc.*, 2437 (1957); M. C. R. Symons, *ibid.*, 2440 (1957).

(24) (a) J. C. D. Brand and J. R. Davidson, *ibid.*, 15 (1956); R. E. Davis and C. Perrin, Abstracts of Papers, Amer. Chem. Soc. Meeting, Boston, Mass., April 5, 1959, p. 87-O; (b) O. Foss, *Acta Chem. Scand.*, 307 (1947).

(25) (a) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269, 272 (1946); (b) H. Z. Lecher and E. M. Hardy, *J. Org. Chem.*, **20**, 475 (1955).

The equations have been simplified by including hydrolysis only at the last stage. If thiol and thioaldehyde hydrolyses to alcohol and aldehyde occur fast enough so appreciable concentrations of these species build up, it is assumed that they are oxidized by a mechanism identical to their sulfur analogs.

Since the rate of appearance of final product equals disappearance of arylmethyl compound,[2] the concentrations of all these intermediate oxidation levels must be small and constant. Consistent with this is the fact that the oxidation of a benzyl alcohol is 59 times faster than the comparable arylmethyl compound.[26] Therefore, the above scheme can be simplified to

Activation energies

$$\mathrm{Y_2S}_{n+1} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{YS}_a\cdot + \mathrm{YS}_b\cdot \qquad E_1, E_2 \qquad (14)$$

$$\mathrm{YS_a}\cdot + \mathrm{ArCH_3} \xrightarrow{k_3} \mathrm{YS}_a\mathrm{H} + \mathrm{ArCH_2}\cdot \qquad E_3 \qquad (15)$$

$$\mathrm{ArCH_2}\cdot \xrightarrow[\text{and hydrolysis in excess polysulfide}]{\text{rapid oxidn.}} \mathrm{ArCO_2^-} \qquad E_4 \qquad (16)$$

The assumption of a steady state in the concentration of $\mathrm{YS_a}\cdot$ radicals gives

$$-\frac{\mathrm{d(ArCH_3)}}{\mathrm{d}t} = \frac{k_3(\mathrm{ArCH_3})}{2k_2}\left[-k_3(\mathrm{ArCH_3}) + \sqrt{k_3^2(\mathrm{ArCH_3})^2 + 4k_1k_2(\mathrm{Y_2S}_{n+1})}\right] \qquad (17)$$

It is probable that

$$[(k_3)(\mathrm{ArCH_3})]^2 << 4k_1k_2(\mathrm{Y_2S}_{n+1}) \qquad (18)$$

since $(\mathrm{ArCH_3})^2$ is less than $(\mathrm{Y_2S}_{n+1})$ and k_3 is small. If $k_3^2(\mathrm{ArCH_3})^2$ is neglected in 17, equation 19 results

$$-\frac{\mathrm{d(ArCH_3)}}{\mathrm{d}t} = \frac{k_3(\mathrm{ArCH_3})}{2k_2}\left[-k_3(\mathrm{ArCH_3}) + \sqrt{4k_1k_2(\mathrm{Y_2S}_{n+1})}\right] \qquad (19)$$

The assumption which is made in 18 is equivalent to assuming that $k_3(\mathrm{ArCH_3})$ is much smaller than $\sqrt{4k_1k_2(\mathrm{Y_2S}_{n+1})}$, and therefore equation 19 reduces further

$$-\frac{\mathrm{d(ArCH_3)}}{\mathrm{d}t} = \frac{\mathrm{d(ArCO_2^-)}}{\mathrm{d}t} = \left(\frac{k_1}{k_2}\right)^{1/2} k_3(\mathrm{ArCH_3})(\mathrm{Y_2S}_{n+1})^{1/2} \qquad (20)$$

which is consistent with the observed rate dependence.

Salt Effect.—It is important to show that the salt effect on k is small since the ionic strength has not been kept constant in these studies. It was found that 1.0 M NaCl produced no change in k (Table III, runs 73, 365, 530). A reaction involving free radical intermediates would be expected to show very small salt effects.

Dependence of k on n and the Energy of S–S Bonds.—The rate of oxidation has been found to be almost proportional to n, the number of S–S bonds in the average polysulfide molecule present. If all S–S bonds have similar energy, the forward rate of reaction 14 would be proportional to the number of such bonds because of a statistical factor.

There is considerable evidence[27–33] that all S–S bonds have an energy of about 53 kcal.[27] for the polysulfides $\mathrm{H_2S}_x$ over the range of x from 1 through 6, and that this energy is independent of x. Surprising in view of this uniformity is the fact that very long chain polysulfides show a much lower bond energy: for a chain 5×10^4 atoms long, the energy drops to 33.4 kcal.[31] This is presumably due to resonance of the radical by expansion of sulfur's octet through use of d-orbitals. In $\mathrm{H_2S_6}$, the average radical is H–S–S–S · which apparently possesses negligible delocalization energy. Therefore, over the range of chain lengths accessible in this study, the dependence of the observed rate constant on number of S–S bonds is quite reasonable. There is evidence from a complex kinetic analysis suggesting that, over the range of bonds lengths 1 through 8, small differences in bond energy may be found.[34]

Activation Energy.—The energy of activation E predicted by the proposed mechanism is

$$E = \frac{1}{2}(E_1 - E_2) + E_3 + E_4 = \frac{1}{2}\Delta H_1 + E_3 + E_4 \qquad (21)$$

where E_4 is equal to the sum of activation energies of reactions 3 through 13. Reaction 14 has E_1 for the forward step equal to about 53 kcal. as discussed above, and for the reverse step $E_2 \simeq 0$, so $\Delta H_1 \simeq$ 53 kcal. The value for E_3 is 0–5 kcal.[16] Thus, the mechanism predicts E is about $(53/2 + 2 + E_4) = (29 + E_4)$ kcal., and the experimental values are in the range of 29–34 kcal.[2] The prediction is in agreement with experiment if E_4 is from 0 to 5 kcal. This is probable because most of the equations 3–13 are reversible and require similar activation energy in either direction and, furthermore, most have small E even if irreversible. For example, a displacement reaction on an S–S bond like equation 3 has $E \simeq 3$ kcal.[31] Note that if equation 14 is not reversible E_1, rather than $^1/_2\ \Delta H_1$, occurs in equation 21; and this would predict an over-large E. This is confirmation that equation 1 is reversible, which was postulated to explain the square root dependence on polysulfide.

Free Radical Mechanisms in Other Reactions of Sulfur.—Lastly, it should be pointed out that the square root dependence of the rate on the concentration of polysulfide is not conclusive that the reaction involves free radicals. The kinetics could be explained as well by a mechanism involving fission of polysulfide to sulfenium and sulfide ions. A recent publication on the reaction of sulfur with olefins at 140° adopts this ionic mechanism although

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half-order rate laws are observed.[35] Square root rate dependence has also been taken as evidence for radical intermediates in other reactions of sulfur.[36] Relative rate studies of a series of arylmethyl compounds give support to the hypothesis that the oxidation studied here involves free radicals.[26] However, it should be pointed out that sulfur-olefin reactions in hydrocarbon solvents at 140° and polysulfide oxidation in aqueous solution at 300° may differ drastically in mechanism.

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[CONTRIBUTION FROM THE IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION, RESEARCH DEPARTMENT]

The Mass Spectrum of Trimethylhydrazine

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The high resolution mass spectrum of trimethylhydrazine is given and is shown to differ in several respects from the previously published low resolution spectrum. In particular, several peaks which were considered to be singlets have now been shown to be multiplets.

The mass spectra of hydrazine and the methyl substituted hydrazines recently have been reported by Dibeler, Franklin and Reese.[1,2] The information obtained, regarding relative abundances and appearance potentials of the principal ions, has been used to estimate heats of formation and probable ionization processes. The empirical formulas of the various ion species have been suggested to be those which would be formed in the most direct processes, and it has been assumed further that only a single ion species contributed to the peak at a particular mass number.

TABLE I

MASS SPECTRUM OF TRIMETHYLHYDRAZINE

(Ions containing C^{13}, N^{15} or D are only listed when they form the major contribution to the peak)

Mass	Relative abundance (%)	Formula
14	2.2	CH_2
15	26.2	CH_3
16	0.12	NH_2
	4.4	CH_4
17	0.33	NH_3
18	14.7	NH_4
26	0.09	CN
	0.24	C_2H_2
27	1.3	CHN
	1.8	C_2H_3
28	16.4	CH_2N
29	2.2	HN_2
	1.2	CH_3N
	2.4	C_2H_5
30	51.5	CH_4N
31	6.9	CH_5N
32	11.3	CH_6N
36	3.3	$C_3H_8N_2^{++}$
36.5	0.89	$C_3H_9N_2^{++}$
38	0.18	C_3H_2
39	0.30	C_3H_3
40	0.72	C_2H_2N
41	1.3	C_2H_3N
42	0.18	CH_2N_2
	59.5	C_2H_4N
43	8.3	CH_3N_2
	8.3	C_2H_5N
44	0.24	CH_4N_2, $C^{13}H_3N_2$ $CH_3N^{14}N^{15}$
	14.3	C_2H_6N
45	1.4	C_2H_7N
46	2.9	C_2H_8N
57	11.3	$C_2H_5N_2$
58	2.2	$C_2H_6N_2$
59	100	$C_2H_7N_2$
60	3.7	$C^{12}C^{13}H_7N_2$ and $C_2H_7N^{14}N^{15}$
71	15.6	$C_3H_7N_2$
72	25.2	$C_3H_8N_2$
73	3.3	$C_3H_9N_2$
74	91.2	$C_3H_{10}N_2$
75	4.9	$C_2{}^{12}C^{13}H_{10}N_2$ and $C_3H_{10}N^{14}N^{15}$

In the course of an investigation in these laboratories we had occasion to plot the spectrum of trimethylhydrazine in a Metropolitan-Vickers M.S. 8 double-focussing mass spectrometer.[3] We took, therefore, the opportunity of measuring the empirical formulas of all ions in the spectrum under conditions of high resolution with the aid of accurate mass measurements.[4] It was found that the spectrum obtained was dependent on the temperature of the inlet line. Figure 1 shows three spectra on low resolution which were also obtained corresponding to temperatures of (a) 180°, (b) 140° and (c) 90°. At temperatures below 90° little change could be detected in the spectrum, so that spectrum of the undecomposed sample was assumed to be the one shown in Fig. 1c.

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