TABLE VI

DETERMINATION OF THE MAGNETIC MOMENT OF Fe(III) IN $(TETA)Fe(OH)_2^+$

[TETA] = 1.0 *M*, temp. = 15°

[Fe(III)] × 10^3 (mole l.$^{-1}$)	*p*H	ΔW (mg.)	Molar paramagnetic susceptibility × 10^6	Magnetic moment (Bohr magnetons)
1.02	8.6	0.289 ± 0.028	11800	5.3
1.02	9.6	.318 ± .022	12600	5.4
2.04	8.6	.576 ± .021	11900	5.3
2.04	9.6	.712 ± .019	14500	5.8
			Av.	5.4 B.M.

TABLE VII

MAGNETIC TITRATION OF $(TETA)Fe(OH)_2^+$ BY CYANIDE

[TETA] = 1.0 *M*, [Fe(III)] = 2.04 × 10^{-3} *M*, *p*H 9.0 ± 0.1

Total added KCN × 10^3 (for. wt./l.)	ΔW (mg.)	Total added KCN × 10^3 (for. wt./l.)	ΔW (mg.)
None	0.713	5.50	0.328
2.00	.549	6.00	.257
2.52	.513	6.52	.215
3.00	.497	7.02	.150
3.51	.479	7.54	.112
4.00	.328	8.00	.143
4.52	.412	10.0	.120
4.98	.294	11.0	.111
5.02	.288	12.0	.128
5.26	.465		

bility of these rather concentrated catalyst solutions, the accuracy of these magnetic data is much lower than the inherent accuracy of the apparatus.

The data in Table VI show that $(TETA)Fe(OH)_2^+$ is in high-spin state, because the measured moment of 5.4 B.M. compares favorably with the calculated moment of 5.92 B.M. for five unpaired electrons per Fe(III) without orbital contribution.

The data in Table VII show that the molar paramagnetic susceptibility of the catalyst decreases as cyanide is added to the solution. In principle, one could plot the values of *W* in Table VII *vs.* total added KCN and determine formation constants of the mono- and dicyanide complexes from the resulting curve by the same procedure which we used to treat the rate data in Table V. Unfortunately the data in Table VII are not suitable for such treatment because of the large experimental uncertainties. However, since the observed molar susceptibility of the catalyst continued to decrease as more KCN was added to the solution, we may still conclude the compound $(TETA)Fe(CN)_2^+$ to be a low-spin complex.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION]

Kinetics of the Oxidation of *m*-Toluic Acid to Isophthalic Acid by Aqueous Sulfur Solutions[1]

BY WILLIAM A. PRYOR

RECEIVED JULY 14, 1958

The kinetics of the oxidation of *m*-toluic acid to isophthalic acid are reported at 230–290° for three aqueous oxidizing systems: sodium polysulfide, ammonium polysulfide and sodium hydroxide plus sulfur. *m*-Toluic acid is always present in limited concentration, and under these conditions the reaction is pseudo-unimolecular with first-order dependence on the concentration of *m*-toluate ion. The reaction is quantitative, and the rate of appearance of product equals the rate of disappearance of *m*-toluate ion. There is no induction period. Rate dependence on the true concentration of any one sulfur species is difficult to measure since most sulfur anions are interconvertible through disproportionation reactions at these temperatures. However, data are consistent with a mechanism in which a polysulfide radical abstracts a benzyl hydrogen atom in the slow step. Possible analogies to vulcanization and to the Willgerodt reaction are discussed.

Introduction

Oxidation of organic materials by sulfur has been known for many years. In vulcanization, a reaction nearly 120 years old, rubber is oxidized by sulfur. Another classical example is the reaction Willgerodt discovered in 1887, in which acetophenone is converted to a mixture of phenylacetamide and ammonium phenylacetate by ammonium polysulfide.[2a] Willgerodt also found sodium polysulfide oxidized acetophenone to sodium phenylacetate, although in very poor yield.[2b] A considerable amount of work has shown a rearrangement is not involved in the Willgerodt reaction.[3]

This reaction, or a modification of it using morpholine as base, has been applied to oxidize compounds containing virtually every possible functional group α to a benzene ring.[2] However, early attempts to extend the reaction to the oxidation of aryl methyl groups failed.[2a]

Recently it has been shown that at higher temperatures, aryl methyl groups can be oxidized and

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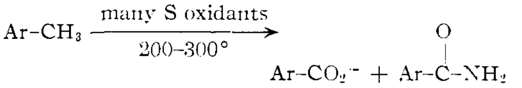
(1) Presented at the Symposium on Recent Developments in Chemicals from Petroleum, 133d Meeting of the American Chemical Society, Division of Petroleum Chemistry, San Francisco, California, April, 1958. Research supported by Oronite Chemical Company.

(2) (a) For review and references to early work see: M. Carmack, M. A. Spielman, R. Adams, Ed., "Organic Reactions," Vol. III, John Wiley and Sons, New York, N. Y., 1946, p. 83; (b) C. Willgerodt and F. H. Merk, *J. prakt. Chem.*, [2] **80**, 192 (1909); (c) M. Carmack and D. F. DeTar, THIS JOURNAL, **68**, 2029 (1946); (d) R. T. Gerry and E. V. Brown, *ibid.*, **75**, 740 (1953); (e) J. A. King and F. H. McMillan, *ibid.*, **68**, 1369 (1946); (f) F. H. McMillan and J. A. King, *ibid.*, **70**, 4143 (1948); (g) W. G. Dauben and J. B. Rogan, *ibid.*, **78**, 4135 (1956); (h) P. A. Barrett, *J. Chem. Soc.*, 2056 (1957).

(3) W. G. Dauben, J. C. Reid, P. E. Yankwich and M. Calvin, THIS JOURNAL, **72**, 121 (1950); E. V. Brown, E. Cerwonka and R. C. Anderson, *ibid.*, **73**, 3735 (1951); J. A. King and F. H. McMillan, *ibid.*, **68**, 633 (1946).

that the reaction has wide scope and great utility.[4c] For example, toluene can be oxidized to benzamide,[4a] the toluic acids are converted to the corresponding phthalic acids,[4b] and the xylenes can be oxidized to phthalic acids.[4c] Virtually any base and any sulfur solution has been found effective.[4c] Amides as well as acids are produced if amines are used as the base. The oxidation of these aryl


(1)

$$Ar{-}CH_3 \xrightarrow[200-300°]{\text{many S oxidants}} Ar{-}CO_2^- + Ar{-}\overset{\overset{\displaystyle O}{|}}{C}{-}NH_2 \qquad (1)$$

methyl substrates seems a simpler reaction than the Willgerodt since it does not involve migration of an oxidized function or reduction of an initially present group. Nevertheless little is known about the detailed mechanism of any of these oxidations using sulfur.

This work describes the beginning of a kinetic study of the mechanism of the oxidation of aryl methyl groups by aqueous solutions of sulfur ions. *m*-Toluic acid was chosen as substrate because of its solubility and non-volatility from aqueous alkaline solutions. Kinetic runs were done in an 8-ml. microbomb[5] heated very rapidly by passing alternating current through the bomb walls. The microanalytical method uses *m*-toluic acid-C^{14} as starting material, paper chromatography of the reaction mixture and measurement of the distribution of radioactivity on the paper chromatogram with a liquid scintillation counter (LSC).

Experimental

Large Scale Preparative Run.—Examples of this reaction have been given by Toland and co-workers.[4b,c]

Microbomb.—The detailed description of the microbomb designed for this work is published elsewhere.[5]

Synthesis of *m*-Toluic Acid-C^{14}.—A Grignard reagent was prepared[6] from Eastman Kodak white label *m*-bromotoluene which contained less than 1.5% *para*-isomer (by infrared spectra and gas–liquid partition analysis) as its only impurity. This was carbonated in a high vacuum line with CO_2 generated from 5 millicuries, 8.1 millimoles of barium carbonate.[7]

The product was homogenized with 9 g. of purified Eastman Kodak white label *m*-toluic acid, m.p. 111.6–112.3°. The radioactive acid was neutralized carefully with sodium hydroxide in 100 ml. of water, filtered, reprecipitated with HCl and finally recrystallized from water. Eight grams of *m*-toluic acid was obtained, m.p. 111.4–112.0° (melting points corrected). Calcd.: C, 70.57; H, 5.92. Found: C, 70.37; H, 5.98; Cl, 0.0.

Sulfur Compounds.—Sulfur purified[8] by boiling with MgO (55 parts per million Mg is chief impurity) or sublimed sulfur (5 p.p.m. Mg, 7.6 p.p.m. Si, 4.0 p.p.m. Fe and less than 0.1% organic material) gave the same rate. Baker $Na_2S \cdot 9H_2O$ and ammonium sulfide ("light") were used. Solutions were prepared from boiled water, were protected with nitrogen blankets and kept in nitrogen flushed flasks.

Sulfur Analysis.—The complete analysis of an aqueous polysulfide solution includes analysis for polysulfide-sulfur, sulfide, thiosulfate and sulfate. Sulfite is converted to thiosulfate in the presence of polysulfide.[9] Analysis is done by determining polysulfide-sulfur polarographically[10a] or by a titration procedure in which polysulfide-sulfur is first converted to thiocyanate.[10b] The latter is more accurate in the presence of thiosulfate. Sulfide plus thiosulfate is determined iodimetrically.[11] Thiosulfate is determined by precipitating zinc sulfide, filtering and titrating the filtrate with iodine.[11] Sulfide is then measured by treating the zinc sulfide precipitate with acid and titrating with iodine.[11] Sulfate is measured by acidifying to *p*H 1, precipitating $BaSO_4$ at 100° with $BaCl_2$ (10 ml. of 10% solution), coagulating on the steam-plate for 2 hours, filtering and igniting at 800°.

Analysis for Radioactive Materials.—A 15–50 λ aliquot is pipetted from the reaction mixture onto a 1-inch by 20-inch strip of Whatman No. 4 paper. The paper is hung in a chromatographic cabinet and the material allowed to elute downward. The solvent is 10-ml. concentrated ammonium hydroxide diluted to 100 ml. with absolute ethanol. The R_F values are 0.68 for *m*-toluic acid and 0.05 for isophthalic acid.[12] Acids were located by dying the paper with brom phenol blue, scanning the paper with a 2-inch diameter mica window Geiger tube (Anton Electronic, Brooklyn, New York, No. 1001T) or placing X-ray film[13] over the chromatogram in a light-proof press for three days to several months and then developing it. All three methods agree in locating spots.

Only semi-quantitative analysis could be obtained using the Geiger tube, probably due to difficulty in reproducing geometry when counting an irregular size spot on filter paper. To determine the distribution of activity quantitatively, a liquid scintillation counter (Tracerlab, Model CE-1) is used.[14] The areas of the paper containing the *m*-toluic and isophthalic acid are cut from the paper and separately shredded into 40-mm. by 80-mm. glass-stoppered weighing bottles. All the rest of the strip is shredded into a third jar. Ten milliliters of a solution of 0.1 ml. of HCl and 4.9 ml. of water diluted to 100 ml. with absolute ethanol is added to each jar and the paper allowed to soak for one-half hour. This removes the compounds from the paper. Then, 50 ml. of toluene is added which contains 18.0 mg. of α-naphthylphenyloxazole and 4.79 g. of diphenyloxazole per liter of toluene.[11] These jars are placed in an ice-box at −10°, allowed to dark-adapt and then counted. Neither brom phenol blue nor any of the reaction products affect counting efficiency. The HCl is necessary for desorption of the acids from paper but also does not affect counting. The per cent. recovery of activity is calculated by comparing total activity from a run with the activity found for a standard *m*-toluic acid solution.

When ammonium polysulfide is used, amides must be hydrolyzed before analysis. A 3-ml. aliquot of the reaction solution is pipetted into a centrifuge tube; 10 ml. of water and about 0.75 g. of sodium hydroxide are added. The solution is heated for about 24 hours at 90° until ammonia is no longer evolved. The solution is then concentrated to 5–7 ml. and a 50–100 λ aliquot used to prepare the paper chromatograms.

Kinetic Procedure.—Each point in a kinetic run is a separate bomb experiment. Zero time is the time when reaction temperature is first reached. The final time is taken as the time when an air jet is turned on which cools the bomb at 5° per second. The total volume of all reactions was 4.00 ml. at 25°, 5.33 ml. at 288°. Volume changes can be ignored since first-order rates are being measured and only (m/m_0), the fraction *m*-toluate remaining need be evaluated.

Reproducibility of Kinetic Runs.—The largest sources of error are temperature control and LSC counting. Each of

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TABLE I

OXIDATION OF SODIUM *m*-TOLUATE BY AQUEOUS SODIUM POLYSULFIDE[a]

Run no.	Min. at temp.[c]	Mmoles added NaOH	S	Toluic	Na_2S	Activity distribution on chromatogram, % Toluic	IP[d]	$k \times 10^4$, sec.$^{-1}$	Recovery of activity, %
58	25	0.188	4.6[e]	0.188	2.1	68.4	30.9	2.52	103
72	45	.194	4.6	.094	2.1	54.0	45.2	2.22	120
63	60	.188	4.6	.188	2.1	44.3	55.2	2.26	111
70	60	.094	4.6	.094	2.1	41.5	57.1	2.44	110
76	140	.094	4.6	.094	2.1	10.9	88.7	2.65	120
							Av.	2.42 ± 0.14	
90[c]	100	0.088	4.6	0.088	2.1	57.6	40.5	0.918	85
91[c]	100	.175	4.6	.175	2.1	60.4	38.8	0.839	95
							Av.	0.88	
66	32	0.188	2.3	0.188	1.0	74.6	24.9	1.52	111
62	40	.188	2.3	.188	1.0	67.2	31.8	1.66	105
71	60	.092	2.3	.092	1.0	55.8	43.1	1.62	104
60[b]	84	.188	2.3	.188	1.0	48.9	50.3	1.46	110
59	84	.188	2.3	.188	1.0	47.6	51.8	1.47	95
							Av.	1.55 ± 0.07	
77	35	0.094	6.9	0.094	3.2	48.0	50.3	3.49	109
78	30	.094	6.9	.094	3.2	54.5	43.6	3.37	111
							Av.	3.43	
79	19	0.094	9.2	0.095	4.2	62.1	37.3	4.26	102
80	16	.094	9.2	.095	4.2	68.6	30.4	4.03	87
							Av.	4.15	

[a] All runs are 4.00 ml. solution at 25°. [b] No agitation. [c] Temperature is 288° for all runs except no. 90 and 91 where it is 266°. [d] Abbrev.: IP = isophthalic acid. [e] *I.e.*, 147 mg. sulfur.

these introduces up to 3% scatter in the data. Duplicate kinetic runs generally agreed within 4%, which is considered satisfactory in view of the high temperatures and pressures involved.

Homogeneity of the Reaction.—The oxidation by NaOH + S and by $Na_2S_{3.2}$ proceeded at the same rate whether the bomb was unshaken or agitated at 1000 cycles per minute. These reactions are undoubtedly homogeneous. Both sodium and ammonium polysulfide solutions are homogeneous when added to the bomb and when removed, and it is probable they remain homogeneous during reaction.

Results

In the oxidation of *m*-toluic to isophthalic acid, it is convenient to use excess sulfur oxidant. Then the concentrations of sulfur species are not appreciably altered by reaction with organic materials, and independent studies of the sulfur system can be correlated with rate measurements. This is an advantage since the inorganic system is complex with sulfur anions of different oxidation levels interconvertible at these temperatures through disproportionation reactions.[15-17]

When excess oxidant is used, the dependence on *m*-toluic acid is pseudo-unimolecular with smooth first-order dependence on the concentration of *m*-toluate ion. A positive but non-integral dependence is found on total sulfur added (see below).

The kinetics reveal several facts about the organic system. First, no product is formed other than isophthalic acid. The reaction is quantitative, and there is no buildup of any intermediate. The rate of formation of isophthalic acid equals the rate of disappearance of *m*-toluic acid. Second, the kinetics show no induction period. The graphs showing first-order dependence extrapolate through the origin. Third, all oxidants studied are similar. Rates of oxidation are similar, and kinetic dependence on *m*-toluate ion is the same.

Tables I and II give data for oxidation by sodium and ammonium polysulfide solutions. Figure 1 shows the usual graph for a first-order reac-

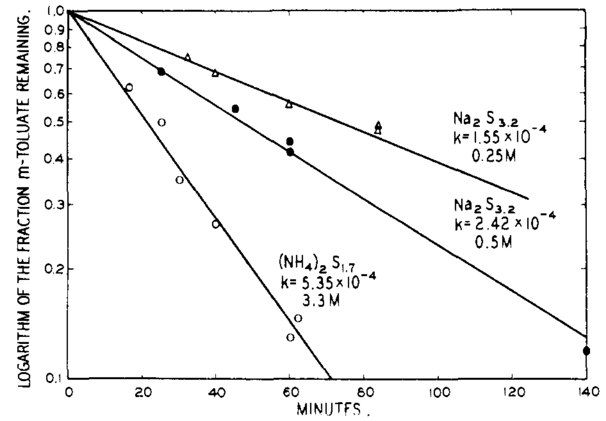

Fig. 1.—Oxidation of *m*-toluate by sodium or ammonium polysulfide at 288°.

[15] E. Schulek and E. Koros, *Magyar Kém. Folyóirat*, **56**, 426 (1950); E. Schulek, E. Koros and L. Maros, *Magyar Tudományos Akad. Kém. Tudományok Osztályának Közleményei*, **7**, 91 (1955); E. Schulek, E. Koros and L. Maros, *Acta Chim. Acad. Sci. Hung.*, **10**, 291 (1956); H. V. Tartar and C. Z. Draves, THIS JOURNAL, **46**, 574 (1924); T. G. Pearson and P. L. Robinson, *J. Chem. Soc.*, 1473 (1930); E. R. Bertozzi, U. S. Patent 2,796,325 (Thiokol Chemical Corporation), June 18, 1957.

[16] R. H. Vallance, D. F. Twiss and A. R. Russell, J. N. Friend, Ed., "Text Book of Inorganic Chemistry," Vol. VII, Charles Griffin and Company, Ltd., London, 1931, Part 2, p. 37.

[17] W. G. Toland, U. S. Patent 2,722,473 (California Research Corporation), November 1, 1955.

tion. The rate constant is unchanged to 90% conversion. Increasing the polysulfide concentration increases the rate constant. Table III gives data using 0.5 *N* NaOH plus a varying molar excess of sulfur. Figure 2 graphs these data for two ratios of sulfur to sodium hydroxide. The rate is first order but slows down beyond about 50% reaction. (Runs 39 and 40 which are not shown in Fig. 2 clearly show *k* decreases.) This probably is due to slow, irreversible formation of sulfate. Despite the rate slowing, first-order dependence is found in sodium *m*-toluate as shown by the constancy of *k* as the initial concentration of *m*-toluate is varied. Increasing the total amount of sulfur added increases the rate.

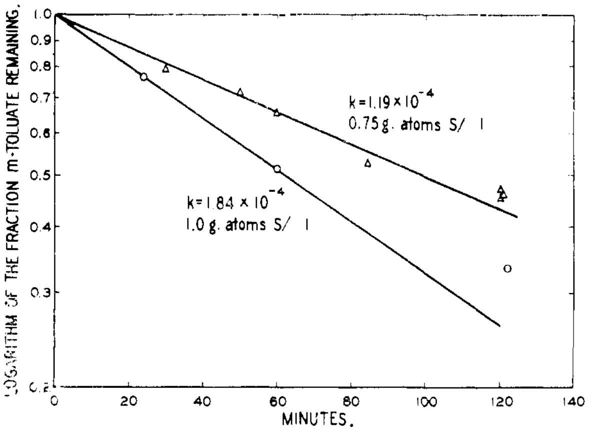

Fig. 2.—Oxidation of sodium *m*-toluate by sulfur plus sodium hydroxide at 288°.

TABLE II

OXIDATION OF AMMONIUM *m*-TOLUATE BY AQUEOUS AMMONIUM POLYSULFIDE[a]

Run no.	Reaction temp., °C.	Min. at temp.	Mmoles toluic acid added	Activity distribution on chromatogram, % Toluic	Activity distribution on chromatogram, % IP[b]	$k \times 10^4$, sec.$^{-1}$	Recov. of activity, %
207	288	15	0.088	62.0	35.0	5.23	96
208	288	25	.088	50.5	43.9	4.59	74
220	288	30	.077	34.8	63.8	5.87	90
206	288	40	.063	26.3	70.0	5.57	82
204	288	61	.086	15.6	84.3	5.25	84
205	288	60	.151	13.0	86.2	5.67	83
					Av.	5.35 ± 0.36	
217	260	91	0.091	53.4	43.6	1.15	93
213	262	56	.092	70.5	27.0	1.05	87
226	255	76	.052	67.8	31.0	0.85	97
228	235	137	.055	90.4	8.7	.124	100
229	235	236	.051	83.0	16.0	.131	96
224	232	240	.065	84.6	14.3	.116	96
225	232	300	.060	82.0	17.0	.111	105

[a] All runs are 4.00-ml. solution at 25°. 10.0 millimoles of sulfur and 13.2 millimoles of $(NH_4)_2S$ added in each case. [b] Abbrev.: IP = isophthalic acid.

Dependence on Sulfur.—Measuring the dependence of the rate on the true concentration of polysulfide, or any other sulfur species, is difficult since most are interconvertible at these temperatures. The mechanism of these disproportionation reactions is not known.

TABLE III

OXIDATION OF SODIUM *m*-TOLUATE BY SULFUR IN AQUEOUS SODIUM HYDROXIDE[a]

Run no.	Min. at temp.[d]	Mmoles added S	Mmoles added Toluic acid	Activity distribution on chromatogram, % Toluic	Activity distribution on chromatogram, % IP[e]	$k \times 10^4$, sec.$^{-1}$	Recov. of activity, %
73	84	2.94	0.092	52.6	45.5	1.27	102
38	30	2.94	.184	79.8	19.5	1.25	97
37	60	2.94	.184	65.7	32.3	1.16	98
106	50	2.94	.084	71.9	26.8	1.10	91
					Av.	1.19 ± 0.06	
36	120	2.94	0.184	47.3	51.0	1.04[b]	96
35	120	2.94	.184	45.0	53.4	1.11[b]	100
43[c]	121	2.94	.184	46.1	51.2	1.07[b]	100
39	243	2.94	.184	30.7	68.8	0.81[b]	102
40	244	2.94	.184	34.2	64.8	0.74[b]	93
55	24	4.05	.184	76.6	21.0	1.83	109
44	60	3.96	.184	51.5	47.0	1.85	101
					Av.	1.84	
42	122	4.05	0.184	33.8	63.9	1.47[b]	103
56	60	5.00	.184	60.6	38.2	2.32	111
50	20	6.04	.184	65.8	32.4	3.49	94
88[d]	120	2.94	.138	72.5	25.3	0.45	76
89[d]	120	2.94	.092	74.6	21.4	0.41	90
					Av.	0.43	

[a] All runs use 4.00 ml. of 0.50 *N* NaOH. [b] Rate has slowed and values not used in average. [c] No agitation. [d] Temperature is 288° in all runs except no. 88 and 89, where it is 266°. [e] Abbrev: IP = isophthalic acid.

If sulfur and a base are heated to 100°, polysulfide and thiosulfate are formed[15,16] (equations 2 and 3). When sulfur is heated to 288° in NaOH, sulfide and thiosulfate are rapidly formed and sulfate is formed slowly. The formation of sulfate may proceed through thiosulfate (equation 4). These disproportionation reactions are very fast relative to

$$4S + 4OH^- = S_2O_3^= + 2HS^- + H_2O \qquad (2)$$

$$HS^- + xS = HS_{x+1}^- \qquad (3)$$

$$S_2O_3^= + OH^- \longrightarrow SO_4^= + HS^- \qquad (4)$$

oxidation of substrate, and therefore sulfur plus NaOH oxidizes very much as does preformed sodium polysulfide.

To determine whether polysulfide concentration can be correlated with the rate of oxidation, the steady state concentration of polysulfide in solution at 288° is necessary. This requires correcting for sulfur used and sulfide formed through equations 2–4, and also for the varying fraction of sulfide in the vapor as H_2S. For the NaOH plus S oxidant, the correction due to equations 2–4 is very large. For the preformed polysulfide oxidants, where the initial hydroxide concentration is lower, this correction is smaller and the total added polysulfide is a good approximation to the actual polysulfide present at 288°.

Calculations from the data of Table I give the order in total polysulfide added as 0.7. Experiments in which the dissolved polysulfide at temperature is measured and studies of the sulfur disproportionation reactions are in progress.

Other Products.—Better than 98% of the activity added can be accounted for as isophthalic and *m*-toluic acids. The balance of the activity is due to two random sources of error. The first is contamination of the entire chromatogram. When *m*-toluic acid knowns are chromatographed, 1.0 ± 0.5% of the activity is spread diffusely outside the *m*-toluic acid spot. This is the limit of the chromatographic procedure. The second is retention of activity at the origin, undoubtedly by occlusion in the sulfur cake which does not move down the chromatogram. When polysulfide solutions are chromatographed with *m*-toluic acid knowns, occasionally activity is trapped in the sulfur cake.

Kinetic runs showed extraneous activity from both these sources. For example, the average extraneous activity found is 1.0% for sodium polysulfide oxidation. However, many runs showed only 0.5% or less extraneous activity. The ability to detect easily this occluded activity insures that any intermediates or by-product present in about 0.2% would show as discrete, reproducible spots on films made from chromatograms and none are found.

Activation Energy.—The Arrhenius activation energy is 29 kcal. for both the sodium polysulfide and the NaOH + S oxidants studied. Over a comparable temperature range, the ammonium polysulfide oxidation gives E_a as 34 kcal.; if data at 232° are included, the value is 39 kcal. Other sodium polysulfide solutions, not reported here, give E_a from 29 to 35 kcal. The magnitude of E_a apparently depends on the ratio of cation to sulfur and perhaps also on the nature of the cation. These variables affect the equilibria reactions which precede the step with the smallest rate constant.

Discussion

Although more information is required to answer many questions about the mechanism, some features seem clear. The similarities in the oxidizing solutions used make it likely that one general mechanism is operating.

The mechanism is probably radical and not ionic and involves polysulfide radicals abstracting a benzyl hydrogen atom. An alternate mechanism, involving base removing a proton and the resulting carbanion attacking sulfur, is not likely for the following reasons. In runs such as 73, Table III, the concentration of hydroxide changes from 0.5 to 10^{-7} *N* within 5 minutes, but the rate of oxidation is unchanged. Further, sulfur plus any nucleophile, even water alone[4c] or anhydrous morpholine,[2] is an effective oxidant. It appears that the nucleophile promotes opening of the S_8 ring to produce polysulfides.[9c,15–18] The polysulfide then undergoes fission to yield radicals which are capable of abstracting benzyl hydrogens.[19] The similarities in rate and kinetic dependence for oxidation by ammonium or sodium polysulfide solutions are evidence that an ammonium base does not attack the substrate in a critical step. Such a mechanism has been suggested for the Willgerodt reaction.[2g,h]

Base catalysis is found for all oxidations by sulfur studied to date,[18,20] but this is not necessarily evidence against a radical abstraction of hydrogen. The S_8 ring is resonance stabilized[21] and is opened by both nucleophiles[9c,18] and radicals.[22] Once opened, linear polysulfides can undergo fission to radicals more easily than can the S_8 ring.

In the sulfur oxidation of aryl methyl compounds, abstraction of the first hydrogen atom is probably the step with smallest rate constant. This is supported by the very low steady state concentration of compounds of intermediate oxidation level found here. It is made additionally probable since any substituent on the side chain permits the oxidation to occur 100–150° lower than for the unsubstituted aryl methyl.[2] The Willgerodt reaction also may involve abstraction of a hydrogen as the first step, since it has been shown that an aryl methyl ketone can be oxidized to an α-keto acid without reduction of the carbonyl.[2g,k]

A mechanism in agreement with these data is reversible fission of polysulfide to two sulfide radicals which attack the methyl group in a step with the smallest rate constant (equations 5–7). This predicts first-order dependence on substrate and 0.5 order on the actual concentration of polysulfide. The value of 0.7 for total added polysulfide is not in extreme variance with this prediction. The dependence on actual steady-state concentration of polysulfide is under investigation as discussed above.

$$\mathrm{YS}_x\!-\!\mathrm{S}_x\mathrm{Y} \rightleftarrows 2\mathrm{YS}_x\cdot \qquad (5)$$

$$\mathrm{YS}_x\cdot + \mathrm{ArCH_3} \rightleftarrows \mathrm{YS}_x\mathrm{H} + \mathrm{ArCH_2}\cdot \qquad (6)$$

$$\mathrm{ArCH_2}\cdot \xrightarrow[\text{and hydrolysis}]{\text{oxidn. by polysulfide}} \mathrm{ArCO_2}^- \qquad (7)$$

where Y can be Na, NH_4, H, $ArCH_2$, etc.

Several other examples of sulfur abstracting active hydrogen are known. At 100–140°, sulfur reacts with olefins to form an adduct which then adds to a second olefin molecule.[23] There is no direct evidence on whether the hydrogen abstraction is ionic or radical,[24b,d] although radical seems favored.[23,24e] The subsequent reaction definitely appears to be ionic addition of a mercaptide ion to a double bond.[24,25] Bases catalyze the reaction of sulfur with olefins. However, when nitrogen bases are used, the evidence for radical reactions is even less clear cut.[26]

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(20) The reaction of thiols with sulfur to produce disulfides and H_2S shows enormous catalysis by bases but none by benzoyl peroxide (ref. 2f). Also, see G. F. Bloomfield, *J. Soc. Chem. Ind.*, **67**, 14 (1948).

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(25) Ref. 19, p. 315; S. O. Jones and E. E. Reid, THIS JOURNAL, **60**, 2452 (1938).

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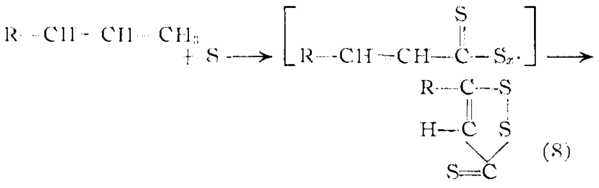
At 200°, similar substrates give 1,2-dithiole-3-thiones,[27] as in equation 8. Thiolethiones appear


(8)

to have exceptional stability,[28] and may arise by closure of a dithio acid radical followed by dehydrogenation. This intermediate thio acid radical is similar to those which might exist in the reaction reported here. In the oxidation discussed here, however, intramolecular closure is not possible and hydrolysis yields stable products. Thiolethione formation is also base catalyzed and H_2S pressure increases at a first-order rate. (Calculations based on data of Fields.[29])

Butyl rubber reacts to incorporate sulfur into the rubber hydrocarbon at a rate that is first order in sulfur and zero order in hydrocarbon.[30a] This reaction also is base catalyzed.[30b] The activation energy for vulcanization is roughly 30 kcal.,[30c] and the dissociation energy of a long chain polysulfide is 33 kcal.[31] It would appear, therefore, that the slow step in vulcanization is fission of an S–S bond followed by rapid attack on substrate, giving zero-order dependence on hydrocarbon.[30a] The first-order dependence on substrate found in the reaction reported here is therefore distinctive and indicates attack of the sulfur radical on substrate, rather than production of sulfur radicals, must be rate limiting.

Finally, the reaction of sulfur with diphenylmethane at 200° is of interest. The detailed mechanism is in doubt since results by Moreau[32] at 250° and Tsurugi[33] at 200° are in contradiction. Both find thiobenzophenone as final product but Tsurugi finds benzhydryl polysulfide is an intermediate, H_2S pressure increases at a first-order rate, the reaction is accelerated by light and the reaction is base catalyzed.[33]

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The Reactions of Perfluoro-*n*-propyl Radicals with Hydrogen and Deuterium

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Perfluoro-*n*-propyl radicals were produced by the photolytic decomposition of perfluoro-di-*n*-propyl ketone using 3130 Å. radiation. Activation energies for the reactions $C_3F_7 + H_2 \rightarrow C_3F_7H + H$ (1) and $C_3F_7 + D_2 \rightarrow C_3F_7D + D$ (2) were found to be 12.3 ± 0.4 and 13.8 ± 0.5 kcal. per mole, respectively. A brief study of the competitive reaction $C_3F_7 + H_2 + D_2 \rightarrow C_3F_7H + C_3F_7D +$ etc., has shown the difference in activation energies between reactions 1 and 2 to be 1.7 kcal. per mole.

The initial step in the photolysis of perfluoro-di-*n*-propyl ketone has been shown to involve the formation of n-C_3F_7 radicals, the only reaction products being CO and C_6F_{14}.[2] The availability of these radicals makes possible a study of the abstraction reactions

$$C_3F_7 + RH \longrightarrow C_3F_7H + R\cdot$$

A comparison of the activation energies and steric factors of these reactions with the corresponding reactions for CF_3, C_2F_5 and the hydrogenated analogs is of theoretical interest. In this work the n-C_3F_7 radicals have been reacted with hydrogen and deuterium.

Experimental

Apparatus and Procedure.—The apparatus used for these experiments was the same as was used for the previous investigation.[2] Light from a B.T.H. high pressure mercury lamp (type ME/D, 250 watts) was collimated *via* two quartz lenses and a stop. The 3130 Å. radiation was isolated by means of standard nickel chloride, potassium chromate, potassium hydrogen phthalate and Corning 9863 filters.[3] The parallel beam had approximately the same diameter as the completely illuminated cell.

The quartz reaction vessel had a diameter of 5 cm., length of 10 cm. and a volume of 175 ml. It was connected to the vacuum system by means of a specially designed mercury cut-off which was mounted directly below the cell.[4] A small freeze-out trap was connected to the top of the cell.

After the ketone ($C_3F_7COC_3F_7$) was admitted to the cell the pressure was measured by means of a cathetometer focused on a constant-volume manometer. The ketone was condensed at liquid nitrogen temperature until a zero manometer reading was obtained. Hydrogen or deuterium

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