[Contribution from the California Research Corporation]

The Kinetics of Oxidation by Aqueous Polysulfide Solutions. III. The Effect of Substituents on the Oxidation of Arylmethyl Compounds[1]

By William A. Pryor

Received October 3, 1959

A comparison is made of the rates of oxidation by aqueous polysulfide solutions of toluene, *m*- and *p*-xylene, *o*-, *m*-, *p*-toluate salts, and *p*-toluenesulfonate salts. The same relative rate sequence is found for ammonium and sodium polysulfide solutions. The relative rate sequence is very similar to that found when these substrates are attacked by radicals, such as ROO· or Cl·, to abstract a benzyl hydrogen. The rate sequence is the reverse of that found for attack by base at the benzyl position to remove a proton, and the effect of electron-donating substituents on the rate is much less than that found for solvolysis reactions where a negative species is lost from a benzyl position. In addition, the *p*-sulfonate group increases the rate of polysulfide oxidation, contrary to predictions based on its electronic nature. It is therefore concluded that sulfur oxidation occurs by radical attack at the benzyl position by the polysulfenyl radical. A rate comparison is also reported for sulfur oxidation of $ArCH_3$ and $ArCH_2OH$ in which the latter is found to be oxidized 59 times faster than the former. Temperature coefficients for the oxidation of the three toluic acids are given.

Introduction

Aqueous polysulfide solutions oxidize arylmethyl compounds to carboxylic acids at 200–300°. Parts I[2] and II[3] of this series showed this reaction is first order in organic substrate and one-half order in polysulfide oxidant.

The mechanism[3] which best accommodates known facts involves reversible fission of a polysulfide molecule to two polysulfenyl radicals. These radicals then abstract a benzyl hydrogen atom in a step with small rate constant (equations 1–5).

$$Y_2S_{n+1} \underset{2}{\overset{1}{\rightleftarrows}} YS_a\cdot + YS_b\cdot$$

$$YS_a\cdot \text{ (or } YS_b\cdot\text{)} + ArCH_3 \underset{4}{\overset{3}{\rightleftarrows}} YS_aH + ArCH_2\cdot$$

$$ArCH_2\cdot \xrightarrow[\text{fast oxidn. and hydrolysis}]{5} ArCO_2^-$$

where $(n + 1) = a + b$, and Y is Na, H, $ArCH_2$, ArCS, etc. All polysulfenyl radicals (*e.g.*, $NaS_2\cdot$, $NaS_3\cdot$, $HS_3\cdot$, $ArCH_2S_3\cdot$) are considered equivalent in ability to abstract benzyl hydrogens.[3]

An important feature of this mechanism is that fission of polysulfide is postulated to give polysulfenyl radicals. The kinetics would be satisfied equally well by fission to a sulfenium and a sulfide ion. A mechanism of this ionic type recently has been published[4] for reactions of sulfur with olefins at 140° which postulates that sulfenium ions are the active species; the kinetics are complex but involve the square root of the sulfur concentration.

Direct confirmation that radicals are involved in the reaction reported here is desirable but cannot be sought by the usual methods. For example, an attempt to initiate polymerization using this system is not possible because of destruction of the monomer[5] or inhibition by sulfur.[6]

Qualitative evidence that radicals may be involved in this oxidation comes from the observation that the reaction solution passes through a transient blue color. Several systems in which sulfur is blue have been shown to contain radicals by paramagnetic resonance spectra.[7]

Another approach to the problem of the nature of the reaction intermediates is the effect on the rate of substituents on the ring, since cationic, anionic and radical processes respond very differently to substituents. It is this approach which is reported here. Unfortunately under the conditions of the reaction the number of substituents which can be tested is limited. The substituents which will withstand the conditions are carboxyl and sodium sulfonate groups.[8] In the case of the xylenes, the effect of one methyl on the rate of oxidation of the other can be determined, and thus methyl is a usable substituent. All other groups are destroyed by being hydrolyzed, oxidized or reduced during reaction.

Experimental

Techniques[2] and apparatus[9] have been described. The kinetics are followed using radioactive substrates and analysis by liquid scintillation counting of paper chromatograms.[2] For this purpose the radioactive materials in Table I were prepared.

Table I

Radioactive Compounds Synthesized

	Activity[b]	Location of C^{14}-carbon
o-Toluic acid	7.77 c./s./μg.	Carboxyl
m-Toluic acid	29.6 c./s./μg.	Carboxyl
p-Toluic acid	22.5 c./s./μg.	Carboxyl
m-Tolylcarbinol	454 c./s./λ	Carbinol
m-Xylene	161 c./s./λ	Methyl
p-Tolylcarbinol	172 c./s./mg.	Carbinol
p-Xylene	56.3 c./s./λ	Methyl
Na^+ *p*-toluenesulfonate	46.4 c./s./mg.	Random
Toluene[a]	465 c./s./λ	Random

[a] Purchased from Nuclear-Chicago. [b] Counted in a liquid scintillation counter as described[2]; efficiency is about 65%.

Toluic Acids.—The three toluic acids were made by carbonating the appropriate Grignard reagent.[10] Table II gives data on these syntheses.

---

[1] Work supported by Oronite Chemical Co.

[2] W. A. Pryor, This Journal, **80**, 6481 (1958).

[3] W. A. Pryor and L. L. Ferstandig, *ibid.*, **82**, 283 (1960).

[4] G. W. Ross, *J. Chem. Soc.*, 2856 (1958).

[5] J. A. King and F. H. McMillan, This Journal, (a) **68**, 525 (1946); (b) **68**, 2335 (1946); (c) M. Carmack and D. F. DeTar, *ibid.*, **68**, 2029 (1946).

[6] P. D. Bartlett and H. Kwart, *ibid.*, **74**, 3969 (1952); P. D. Bartlett and D. S. Trifan, *J. Polymer Sci.*, **20**, 457 (1956); J. L. Kice, *ibid.*, **19**, 123 (1956); W. E. Mochel and J. H. Peterson, This Journal, **71**, 1426 (1949); G. J. Antfinger and C. H. Lufter, *Ind. Eng. Chem.*, **45**, 182 (1953).

[7] W. A. Pryor, *Chem. Revs.*, to be published; also see note 18, ref. 3.

[8] W. G. Toland, D. L. Hagmann, J. B. Wilkes and F. J. Brutschy, This Journal, **80**, 5423 (1958).

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

[10] See references given in ref. 2.

Xylenes.—*m*- and *p*-Xylene were prepared from *m*- and *p*-toluic acids by the route:

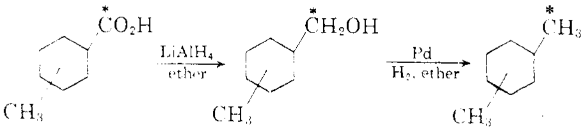


TABLE II

SYNTHESES OF THE THREE TOLUIC-*carboxyl*-C^{14} ACIDS

	Ortho	*Meta*	*Para*
Grignard reaction			
Bromotoluene, mmoles used	30[a]	41[b]	30[c]
Magnesium, mmoles used	33	44	33
Ether, ml. used	60	60	60
Carbonation			
Grignard reagent, mmoles	4.4	9.2	4.4
Ether, ml.	25	20	25
$BaCO_3$, mmoles	4.0	7.3	4.0
$BaCO_3$ mcuries	3.1	5.0	1.9
Inactive toluic acids used as diluent			
M.p.,[d] °C.	104.4–104.6	111.4–112.0	179.4–180.1
G. used	1.00	9.00	1.00
Radioactive acid obtained[e]			
G. before dilution	0.39	1.00	0.40
Mole per cent. yield	72	90	75

[a] Eastman Kodak Co., distilled, b.p. 181.0° (759 mm.); infrared spectrum shows <0.5% *para*, <0.1% *meta*. [b] Eastman Kodak Co., infrared spectrum shows <1.5% *para*, <0.2% *ortho;* gas-liquid chromatography shows 0.0% *ortho*. [c] Eastman Kodak Co., purified by zone melting,[11] m.p. 26.0–26.2°; infrared spectrum shows <1% *meta*, <0.1% *ortho*. [d] All m.p.s corrected. [e] Acids purified by crystallization from methanol–water and sublimation.

TABLE III

RATE CONSTANTS FOR POLYSULFIDE OXIDATION

Substrate[a]	$k \times 10^4$, sec.$^{-1}$ NaOH + S[b] 288°	NaOH + S[b] 260°	$Na_2S_{1.4}$[c] 288°	$Na_2S_{1.4}$[c] 260°	$(NH_4)_2S_{1.7}$[d] 288°
o-Toluic acid	1.11 ± 0.11	0.32	1.10	0.22 ± 0.04	....
m-Toluic acid	1.19 ± 0.06[e]	0.32[e]	1.11 ± 0.18	0.22 ± 0.03	5.35 ± 0.36[e]
p-Toluic acid	1.22	0.38 ± 0.01	1.13	0.27	....
Toluene	0.65 ± 0.20	....	....	....	3.0 ± 0.7
m-Xylene	....	....	....	....	3.8 ± .5
p-Xylene	....	....	....	....	5.0 ± .9
Sodium *p*-toluenesulfonate	0.74 ± 0.07	....	....	....	

[a] Substrate always present at 0.01–0.15 *M*. All rate constants are per methyl group. At least two and usually five runs are averaged. Average deviations are given when more than two runs were averaged. [b] 0.50 *N* NaOH + 0.73 g. atom/l. sulfur; see ref. 2. [c] Prepared by mixing 40.00 ml. of a solution of 3.410 g. of Na_2SO_4, 0.770 g. of sulfur, and 19.80 g. of $Na_2S_2O_3 \cdot 5H_2O$ with 40.00 ml. of a 2.24 *M* NaHS solution. After heating to 90° to dissolve the sulfur, analysis gave 0.96 *M* sulfide, 0.35 *M* sulfate, 0.28 *M* polysulfide-sulfur, and 0.95 *M* thiosulfate, *p*H 8. [d] 3.30 *N* $(NH_4)_2S$ + 2.50 g. atoms/l. sulfur; see ref. 2. [e] From ref. 2.

Tolylcarbinols—*p*-Toluic acid-C^{14} (50.1 mg.) was diluted to 7.15 g. (52.5 mmoles) with inactive acid and dissolved in 300 ml. of dry ether. Lithium aluminum hydride (5.00 g., 230 mmoles) was swirled in 200 ml. of ether and the toluic acid solution added over 5 minutes. After one hour, water and then sulfuric acid were added.[12] The two homogeneous phases were separated and the water phase extracted with ether, the ether concentrated, washed with carbonate and water, and then removed, leaving 5.36 g. (84%) of the *p*-tolylcarbinol-1-C^{14}.

The *p*-carbinol was reduced by dissolving 1.53 g. in 50 ml. of ether which contained 0.42 g. of 5% palladium-on-carbon (Baker and Co., Lot No. 1444). Theoretical hydrogen uptake required 3.5 hours at 25° and 1 atm. Inactive *p*-xylene (3.00 ml. of 99.8% pure by f.p.) was added. Distillation gave 4.3 ml., 3.51 g. (94%), of *p*-xylene-1-C^{14}. Gas–liquid chromatography showed the product to be 97.8% xylene, 1.4% ether, and 0.7% material boiling below ether. No *p*-carbinol or higher boiling material was present.

The synthesis of *m*-xylene-1-C^{14} was identical except the *m*-tolylcarbinol-1-C^{14} was distilled to give 7.56 g. (83%) of material with b.p. 93° (0.80 mm.). Gas–liquid chromatography on the final *m*-xylene showed 99.9% xylene with 0.05% lower boiling and 0.09% higher boiling impurities.

***p*-Toluenesulfonic Acid.**[13]—Uniformly labeled toluene (Table I) (2.00 ml., 187 mmoles) and sulfuric acid (1.25 ml.) were placed in a small tube arranged with Dry Ice finger above it. The tube was heated to 120° for 6 hours until toluene droplets were no longer visible, and allowing ice crystals to grow on the cold finger. The product was recrystallized from Na_2CO_3–NaCl–water and contained 17.0% sodium chloride which was not removed but does not affect the kinetics.[3] Elemental analysis was correct after allowing for the sodium chloride. The ultraviolet spectrum is identical to the reference standard (API Project 44, Serial No. 775) and shows 82% sodium *p*-toluenesulfonate, in agreement with the elemental analysis. No radioactive impurities were present.

Rate Studies.—Measurement of rates was done as before,[2,3] except in the case of toluene and the two xylenes. Here, the volatile substrate was not recovered after reaction, but only the non-volatile acid product. Previous work[2] showed recovered activity is 100 ± 9% of theory, and runs were carried no further than 50% conversion to minimize errors from this source. The rate constant for oxidation of xylene to the toluic acid stage was calculated as

$$k = \left(\frac{1}{\text{sec.}}\right)\left(\frac{1}{2}\right) \ln \left[\frac{(\text{xylene})_0}{(\text{xylene})_0 - (\text{acids recovered})}\right]$$

where $(\text{xylene})_0$ is the initial xylene added and the factor of $^1/_2$ corrects for two oxidizable methyl groups.

All rate constants were shown to be independent of substrate concentration over at least a threefold change, and therefore are first order.

Results

Table III gives most of the data to be discussed. The rate of oxidation of seven compounds was measured in two sodium polysulfide and one ammonium polysulfide oxidants, usually at two temperatures. Table IV gives the activation energies calculated from these data. They show a dependence on the particular oxidant used as observed before.[2]

Discussion

Three possibilities exist *a priori* for abstraction of benzyl hydrogen by any reactant

---

(11) J. D. Dickenson and C. Eaborn, *Chemistry & Industry*, 959 (1956).

(12) W. G. Brown, R. Adams, Ed., "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

(13) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 2nd Ed., 1941, p. 138.

$$\text{carbonium ion} \quad Z^+ + ArCH_3 \longrightarrow ZH + ArCH_2^+ \quad (A)$$

$$\text{carbanion} \quad Z^- + ArCH_3 \longrightarrow ZH + ArCH_2^- \quad (B)$$

$$\text{radical} \quad Z\cdot + ArCH_3 \longrightarrow ZH + ArCH_2\cdot \quad (C)$$

$$ArCH_2^+,\ ArCH_2^- \text{ or } ArCH_2\cdot \xrightarrow{\text{fast}} \text{product}$$

If reactions are chosen in which the step with the smallest rate constant is the reaction with arylmethyl compound, then the over-all rate of appearance of product will be proportional to the rate of attack of Z on the substrate. In the case of sulfur, the three alternative species are: Z^+ = sulfenium or polysulfenium ion, Z^- = sulfide or polysulfide ion, and $Z\cdot$ = thiyl, sulfenyl or polysulfenyl radical.

TABLE IV

ARRHENIUS ACTIVATION ENERGIES FOR POLYSULFIDE OXIDATION

Substrate	E_{act}, kcal. NaOH + S^a	$Na_2S_{1.4}{}^b$
o-Toluic acid	26.6	34.4
m-Toluic acid	28.5	34.6
p-Toluic acid	25.0	30.6

[a] See note *b*, Table III. [b] See note *c*, Table III.

A ring methyl substituent would have a different effect on these three reactions. Methyl, being electron donating, will stabilize a transition state leading to a benzyl cation and hence increase the rate of mechanism A. Conversely, methyl would decrease the rate of mechanism B. The effect of a methyl on a radical reaction, C, is more complex and depends on whether the attacking radical is electrophilic or nucleophilic.[14–17] However, both the peroxy and polysulfide radicals are electrophilic[18] and, therefore, a methyl substituent would increase the rate of attack by either, but to a lesser extent than observed when a positively charged species attacks.

In Table V, the relative rates of polysulfide oxidation are compared with the relative rates of reactions which are representative models for reactions of type A, B and C. The model used for a reaction of type A is the solvolysis of benzyl tosylates and halides. This is not an exact model. Data for the exact model, namely, relative rates of removal of a benzyl hydride by an acid, are not available, although some qualitative work has been reported.[19] The use of the solvolysis[20] reaction as a model assumes that reaction A and reaction 6 have similar substituent effects. In Table V, the tosylate in acetic acid and the chloride in acetone[21] show

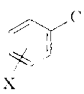
$$ArCH_2X \longrightarrow Ar\overset{+}{C}H_2 + X^- \qquad (6)$$

directionally similar substituent effects, but the better leaving group, tosylate, shows numerically larger effects. When hydride is the leaving group, as in the hypothetical model considered here, the substituent effects may be still smaller,[22] but they will be directionally the same as for tosylate or chloride. Solvolysis is therefore an acceptable approximation to a model reaction of type A.

A good model for a reaction of type B in the abstraction of a benzyl proton by lithium cyclohexylamide in cyclohexylamine,[24] and data for this reaction are given in Table V.

TABLE V

RELATIVE RATE CONSTANTS[a]

 Mechanism	A Carbonium ion		B Carbanion	C Radical		Polysulfide oxidation		
	1 Solvolysis[c]		2	3	4	5		6
X is	Benzyl tosylates	Benzyl chlorides	Benzyl deuterium loss[e]	Oxidation by O_2[f]	Chlorination[g]	NaOH + S[b]	$(NH_4)_2S_{1.7}$[d]	σ[h]
H	1	1	1.00	1.00	1.00	1.00	1.00	0
m-CH_3	2.6	1.2	0.68	1.16	1.33		1.27	−0.07
p-CH_3	56.5	8.7	0.29	1.60	1.62		1.67	− .17
o-CO_2^-	..	..				1.71		..
m-CO_2^-	..	..				1.83	1.78	−0.1[i]
p-CO_2^-	..	(1)				1.88		0[i]
p-SO_3^-	..	(0.65)				1.14		0.1, 0.38[j]
p-Cl	..	0.59		0.84	0.72			0.23

[a] All rates are per methyl group. [b] See note *b* in Table III. [c] See ref. 21, Table 20. Solvolysis of $X-C_6H_4-CH_2OTS$ in acetic acid and $X-C_6H_4-CH_2Cl$ in 50% aqueous acetone. Values in parentheses are calculated from Hammett σρ law using σ from ref. 29, ρ from ref. 30. See note *d* in Table III. [d] See ref. 24; rate of abstraction of deuterium from $ArCH_2D$ by lithium cyclohexylamide in cyclohexylamine. [f] See ref. 14; rate is proportional to removal of benzyl hydrogen by ROO·. [g] See ref. 15; rate is proportional to removal of benzyl hydrogen by Cl·. [h] See ref. 29. [i] Carboxylate σ-values are ±0.1; see Discussion in text. [j] See ref. 30.

An excellent model for a reaction of type C is oxidation by oxygen. There is evidence[14] that, under conditions of high oxygen pressure, the rate of reaction 7 is proportional to the over-all rate of oxidation. For substituted toluenes, where the termination rate is a constant,[14] the relative rates

$$ROO\cdot + ArCH_3 \longrightarrow ROOH + ArCH_2\cdot \qquad (7)$$

---

(14) G. A. Russell, THIS JOURNAL, **78**, 1047 (1956).

(15) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

(16) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); C. Walling and E. A. McElhill, THIS JOURNAL, **73**, 2927 (1951); G. A. Russell and H. C. Brown, *ibid.*, **77**, 4578 (1955).

(17) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

(18) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 417, 318.

(19) E. L. Eliel, P. H. Wilken and F. T. Fang, Abstracts of Papers, 128th Meeting Amer. Chem. Soc., Minneapolis, Minn., Sept. 1955, p. 43-O.

(20) Note unimolecular solvolysis is chosen and not bimolecular displacement. In the latter, nucleophilic attack on carbon is involved rather than electrophilic attack on hydrogen. The choice is important since the relative rate sequence observed is very different for the two types of substitution reactions. See ref. 21, Tables 7, 8, 20, 34.

(21) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1958), Table 20.

(22) Bond breaking will have proceeded less at the transition state when hydride is removed, and consequently substituents will exert less effect.[23]

(23) G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(24) A. Streitwieser, Jr., and D. E. van Sickle, Abstracts of papers, Organic Chemistry Symposium of the Amer. Chem. Soc., June 15, 1959, Seattle, Wash., p. 74.

of oxygen oxidation given in Table V are equal to the relative rates of abstraction of a benzyl hydrogen by the peroxy radical. Table V also gives data for another reaction of type C, chlorination. In this case the rate of reaction is proportioned to the rate of abstraction of hydrogen by chlorine atoms.[15] Columns 3 and 4, Table V, show that H-abstraction by the peroxy radical and the chlorine atom follow very similar relative rate sequences. It seems clear that most electrophilic radicals show rather similar rates of H-abstraction.[25]

Column 5, Table V, gives data for sulfur oxidation. In this case the kinetics[3] suggest the over-all rate is proportional to the rate of reaction 3.

A comparison of columns 1–5 in Table V shows the rate patterns given in Chart 1.[28]

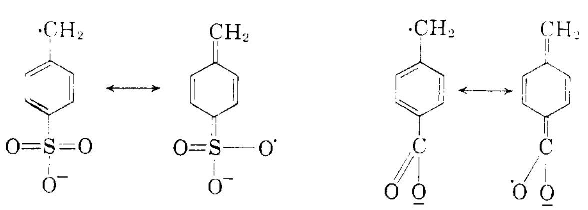
The effect of a *m*- and *p*-methyl substituent on polysulfide oxidation eliminates mechanism B, but does not distinguish between A and C. However, if the quantitative data in Table V are examined, the rate sequence for *m*- and *p*-CH$_3$ and H is almost identical for oxygen oxidation, chlorination and polysulfide oxidation; and this is strongly suggestive that polysulfide oxidation is a free radical reaction, type C. This is not entirely convincing, however, because the rates for loss of hydride rather than chloride or tosylate are not known in mechanism A.

CHART 1

QUALITATIVE EFFECT OF SUBSTITUENTS ON DIFFERENT MECHANISM TYPES

	Mechanism type	Relative rate sequence for ring substituents
A.	Carbonium ion	p-CH$_3$ > m-CH$_3$ > H ~ p-CO$_2^-$ > p-SO$_3^-$
B.	Carbanion	p-CH$_3$ < m-CH$_3$ < H < p-SO$_3^-$
C.	Radical and polysulfenyl oxidation	p-CH$_3$ > m-CH$_3$ > H < p-SO$_3^-$ < p-CO$_2^-$

Examination of the *p*-sulfonate and *m*- and *p*-carboxylate groups provides indicative evidence to distinguish mechanisms A and C. The data show that all of these substituents increase the rate of polysulfide oxidation. The σ-values in Table V indicate *p*-SO$_3^-$ is electron withdrawing, *p*-CO$_2^-$ has no effect, and *m*-CO$_2^-$ is electron donating. If the mechanism for polysulfide oxidation is ionic, these σ-constants lead to the incorrect prediction that each of these three groups should produce a different rate effect. The σ-constants for charged groups such as these vary with the reaction being considered[31] but, qualitatively, an ionic mechanism fails to explain the data. If the mechanism is radical, both *p*-CO$_2^-$ and *p*-SO$_3^-$ can increase the rate by resonance effect, which sometimes opposes the small polar effect found in radical reactions.[32,33] Resonance forms such as those below can increase the rate of a radical reaction by increasing the stability of the transition state.



The lack of *ortho* effect for the *o*-toluate salt could not have been predicted from any of the three mechanisms, but is most consistent with a radical mechanism. If the attacking species were charged, the *o*-carboxylate should give an anomalous rate. Little is known about *ortho* effects on radical reactions, but they may be small. The relative rates of abstraction of a benzyl hydrogen by the *t*-butoxy radical from the three chlorotoluenes are: *o*, 0.73; *m*, 0.70; *p*, 0.85 (relative to toluene as 1)[34a]; the relative rates for hydrogen abstraction by the trichloromethyl radical are: *o*-xylene, 1.02; *m*-xylene, 0.85; *p*-xylene, 0.95.[34b]

A carbonium ion mechanism also is excluded by a comparison of the polysulfide oxidation of toluene and methylpyridines.[7] Both 2- and 4-methylpyridine are oxidized much faster than is toluene, and the 3-isomer is oxidized slightly faster than toluene.[35] These data support either a carbanion or a radical mechanism, but not a carbonium ion mechanism. The ring nitrogen atom can stabilize either a negative charge or an odd electron by resonance forms.[35c,36]

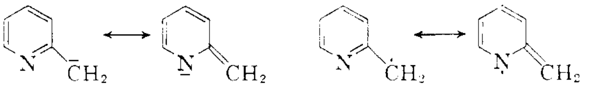


Table V also allows comparison of the rate of oxidation of *m*-toluic acid to toluene in two oxidants, sodium hydroxide plus sulfur and ammonium polysulfide, and the relative rates are found to be the same in both oxidants. The hydrogen donor

---

[25] Russell has argued that there are two different types of radicals, one responding to electron density in the substrate and one to resonance in the transition state as well.[17] The former obeys a $\sigma\rho$-equation with usual values of σ; the latter type follows σ^+ better. The reaction of toluenes with Cl$_2$, and also the reaction reported here, follow σ better than σ^+; and the comparison made in Table V is therefore justified. However, even radicals which give rate sequences correlated by σ^+ (*e.g.*, Br· and ·CCl$_3$)[26] show relative rate sequences rather similar to O$_2$ and Cl$_2$. Another reaction in conformity with a relative rate sequence of type C is chlorination by *t*-butyl hypochlorite which has the sequence: H, 1; *m*-CH$_3$, 1.03; *p*-CH$_3$, 1.40; *p*-Cl, 0.75.[27]

(26) E. C. Kooyman, R. van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **56B**, 75 (1953).

(27) C. Walling, Abstracts of papers, Organic Chemistry Symposium of the Amer. Chem. Soc., June 15, 1959, Seattle, Wash., p. 83.

(28) The values for *p*-SO$_3^-$ and *p*-CO$_2^-$ for type A have been added by predicting the effect of this substituent from its σ-value (Table V, column 6[29]) and the known ρ for the reaction.[30]

(29) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(30) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(31) For example, *p*-SO$_3^-$ gives a σ of 0.38 based on the ionization of ArOH[30] and 0.09 based on the ionization of ArCO$_2$H[29]; also see Y. Okamoto and H. C. Brown, THIS JOURNAL, **80**, 4976 (1958).

(32) D. H. Hey, *J. Chem. Soc.*, 1974 (1952); M. Szwarc, C. H. Leight and A. H. Sehon, *J. Chem. Phys.*, **19**, 657 (1951); M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 245, 278; J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, p. 380.

(33) R. L. Huang, *J. Chem. Soc.*, 1749 (1956); R. L. Huang and S. Singh, *ibid.*, 891 (1958); T. M. Patrick, *J. Org. Chem.*, **17**, 1269 (1952).

(34) (a) K. M. Johnston and G. H. Williams, *Chemistry & Industry*, 328 (1958); (b) E. C. Kooyman and A. Strang, *Rec. trav. chim.*, **72**, 329 (1953).

(35) (a) H. Najer, P. Chabrier, R. Giudicelli and E. Joannic-Voisinet, *Compt. rend.*, **224**, 2935 (1957); (b) H. D. Porter, THIS JOURNAL, **76**, 127 (1954); (c) R. C. Mansfield, *J. Org. Chem.*, **24**, 1111 (1959).

(36) H. S. Mosher in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Editor, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 445, 487; H. C. Brown and W. A. Murphey, THIS JOURNAL, **73**, 3308 (1951).

reactivities in reaction 3 are therefore not strongly affected by the cationic group Y or the value of *a*.

It should be stated explicitly that this mechanism for polysulfide oxidation predicts that the relative rates for reaction 8 will parallel those for this oxidation (Table V, column 5). The thiyl radical can be

$$RS\cdot + ArCH_3 \underset{9}{\overset{8}{\rightleftarrows}} RSH + Ar\dot{C}H_2$$

generated at 25° by photochemical techniques, but as yet a study of reaction 8 has not been made.[37]

There are two oxidations of aralkyl compounds by metal ions that are relevant. The first is the rate of oxidation of aralkyl compounds by potassium permanganate in 54% acetic acid.[38] This reaction is believed to involve attack by a positively charged manganese species.[39,40] The relative rates (per methyl) for substituted toluenes are: H, 1.00; *m*-CH_3, 3.1; *p*-CH_3, 1.6; *o*-CO_2H, 0.89; *m*-CO_2H, 0.54; *p*-CO_2H, 0.48. Here the *o*-CO_2H, even as the neutral acid, has anomalous effect on an ionic reaction. However, this reaction does not show the usual effects of methyl substituents on an ionic reaction.

The second is oxidation of substituted diphenylmethanes by chromic acid in acetic acid. The effect on the rate of *m*-CH_3, *p*-CH_3 and *p*-Cl in that reaction is similar to the other reactions of type C given in Table V and the oxidation is concluded to involve free radical intermediates.[41]

Rate of Oxidation of Carbinol Relative to Methyl.—Another facet of the mechanism proposed involves the nature of steps subsequent to oxidation to the first stage. The very small steady state concentration of intermediates found[2] in the oxidation of *m*-toluic acid suggests that steps after removal of the first hydrogen are relatively fast and that a benzyl thiol or alcohol would be oxidized faster than is toluene.

The rate of oxidation of alcohols is less than or, at most, equal to the rate of oxidation of thiols.[42] It follows that if an alcohol is oxidized too rapidly to be an isolable intermediate, the same must be true of the related thiol.

Therefore, the rate of oxidation of $ArCH_2OH$ and $ArCH_3$ were compared, where Ar is *m*-$CH_3C_6H_4$–. The rate of oxidation of *m*-toluic acid is known[2] at 288° and 200° and Table III gives the rate of oxidation for *m*-xylene at 288°. Assuming the rate of oxidation of both compounds is affected similarly by temperature, the oxidation rate for *m*-xylene at 200° is 0.07×10^{-4} sec.$^{-1}$. This rate for *m*-tolylcarbinol is 4.1×10^{-4} sec.$^{-1}$. It appears, therefore, that the relative rates are: $ArCH_2SH \gtrsim ArCH_2OH\ (\sim 60) > ArCH_3\ (\sim 1)$.

If reaction 3 were not reversible, the mechanism predicts[45] a maximum of 1.5% alcohol is reached in two minutes using these relative rates (ammonium polysulfide oxidant).[2] Experimental results indicate a maximum of 0.2% intermediates is found after 15 minutes.

Acknowledgment.—It is a pleasure to acknowledge encouraging and stimulating discussion with many of my associates and with Professor S. Winstein. Dr. L. L. Ferstandig read the manuscript. Messrs. N. D. McNair and A. J. Clecak gave valuable assistance with much of the experimental work.

---

[37] The detailed kinetics of the reaction between isobutyl thiyl radical and cumene have been reported, however; C. Walling and R. Rabinowitz, THIS JOURNAL, **81**, 1137 (1959).

[38] C. F. Cullis and J. W. Ladbury, *J. Chem. Soc.*, 1407, 2850, 4186 (1955).

[39] J. W. Ladbury and C. F. Cullis, *Chem. Revs.*, **58**, 403 (1958).

[40] L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955); W. A. Waters, *Quart. Revs.*, **12**, 277 (1958).

[41] K. B. Wiberg, Abstracts of Papers, Organic Chemistry Symposium of the Amer. Chem. Soc., June 15, 1959, Seattle, Wash., p. 100.

[42] For example, 1-phenylethyl alcohol[43] and 1-phenylethyl thiol[5a] are oxidized to 48 and 44% of phenylacetic acid, respectively, by aqueous ammonium polysulfide, in 4 hours at 210°. The 2-phenylethyl alcohol and thiol[44] are converted to 0 and 95% of phenylacetic acid, respectively, by aqueous ammonium polysulfide, in 4 hours at 205°.

[43] J. A. King and F. H. McMillan, THIS JOURNAL, **68**, 1369 (1946).

[44] J. A. King and F. H. McMillan, *ibid.*, **68**, 632 (1946).

[45] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 154.

RICHMOND, CALIF.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Thiazolothiazoles. I. The Reaction of Aromatic Aldehydes with Dithioöxamide[1]

BY JOHN R. JOHNSON AND ROGER KETCHAM[2]

RECEIVED NOVEMBER 7, 1959

It has been shown that the reaction of dithioöxamide (rubeanic acid) with aromatic aldehydes is a condensation process involving concurrent loss of two hydrogen atoms. In one instance it was possible to isolate a labile intermediate condensation product that had not undergone dehydrogenation. The two aryl groups in the typical reaction products were shown to be structurally equivalent and the heterocyclic system to be remarkably stable thermally and chemically. A structure having two four-membered heterocycles (VI) has been rejected and the compounds are formulated as aryl derivatives of a new fused heterocyclic system of aromatic character, thiazolo[5,4-d]thiazole (V). The reaction appears to be general for aldehydes of aromatic type, including furfural and cinnamaldehyde. Aliphatic aldehydes and aryl methyl ketones did not furnish condensation products with dithioöxamide.

Ephraim[3] effected the condensation of benzaldehyde with dithioöxamide (rubeanic acid) and obtained in good yield a crystalline product, which was assigned the molecular formula $C_{16}H_{12}N_2S_2$ and represented as 2,2′-diphenyl-4,4′-bithiazetine (I, R = C_6H_5–). The lack of any structural evidence to support this formulation led us to consider two different structures, each containing two fused five-

---

[1] This paper is based upon the doctoral thesis of Roger Ketcham, Cornell University, September, 1956.

[2] National Science Foundation Pre-doctoral Fellow, 1953–1954; General Electric Co. Fellow, 1955–1956.

[3] J. Ephraim, *Ber.*, **24**, 1027 (1891).