0.15 μc. per mmol. equivalent to 15 μc. per mmol. for the undiluted diethyl malonate-2-C^{14} product. Hence, the chemical purity of the diethyl malonate-2-C^{14} was 15/25.7 = 58%, and the weight yield of 100% diethyl malonate based on sodium acetate-2-C^{14} was 0.93 × 0.58 × 36% = 19%. The weight yield of 100% diethyl malonate based on unrecovered ethyl acetate-2-C^{14} was 36 × 0.58/(1.00 − 0.267) = 28.5%.

Acknowledgments.—The author wishes to express appreciation to O. K. Neville and W. G. Brown who made helpful suggestions in the course of this work and to B. M. Tolbert and W. L. Johnson who furnished procedures for the preparation of diethyl oxalacetate.

Summary

Potassium acetate-2-C^{14} has been converted in 76% yield to malonic acid-2-C^{14}. Ethyl acetate-2-C^{14} has been converted to diethyl malonate-2-C^{14} in 28.5% yield. Isotope dilution technique has been applied in studying the reactions involved.

OAK RIDGE, TENN. RECEIVED MARCH 6, 1950

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Mechanism of Aromatic Mercuration.[1] I. Orientation Effects

BY WM. J. KLAPPROTH[2] AND F. H. WESTHEIMER

Introduction

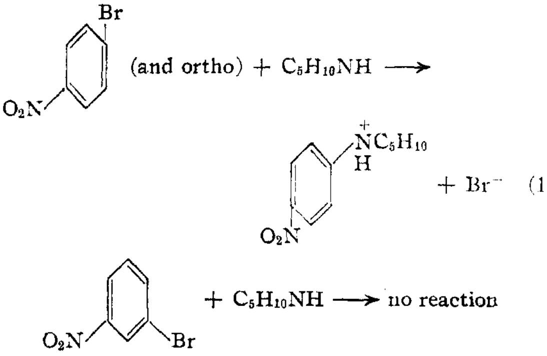
The orientation effects during aromatic substitution are today fairly well understood.[3] During nitration, for example, the OH, NH_2 and CH_3 substituents, present in an aromatic molecule, direct an incoming nitro group to a position ortho or para to the substituent already present, whereas a nitro substituent directs further nitration to the meta position.

It is therefore interesting that mercuration, which occurs quite readily in the aromatic series and which appears (*vide infra*) to be electrophilic substitution, shows a number of anomalies. For although phenol and aniline are mercurated in the ortho and para positions,[4] mercuration of toluene is accompanied by considerable meta substitution,[5] the mercuration of nitrobenzene is reported to be almost random,[6] and mercuration of benzoic acid[7] yields exclusively the compound substituted ortho to the carboxyl group.

It has recently been discovered that mercuration with ionized mercuric salts in strong acid solution[8,9] takes place very much more readily than does the classical mercuration with mercuric acetate in non-polar solvents. It therefore seemed at least possible that the lack of orientation effects in the mercuration of nitrobenzene, etc., was due to the fact that mercuric acetate exists largely, and in non-polar solvents perhaps exclusively, as undissociated molecules, whereas the common electrophilic substituting reagents probably exist either as ions (*e. g.*,[10] NO_2^+) or as highly polarized molecules. The investigations here reported show that mercurations of nitrobenzene and of toluene by mercuric perchlorate in aqueous perchloric acid solutions display the usual orientation effects for electrophilic substitution.

Analytical Methods

The various isomeric mercury compounds obtained on mercuration of nitrobenzene are not readily separable. These compounds were therefore treated with bromine in chloroform solution. This reaction has been shown[11] to lead to replacement, without rearrangement, of the mercury by a bromine atom. The isomeric bromonitrobenzenes can easily be analyzed (for the proportion of meta isomer) by taking advantage of the fact that the halogen atom ortho or para to the nitro group is activated toward replacement reactions, whereas the halogen atom in meta nitrobromobenzene is inert. The reagent chosen for this replacement was piperidine; the sum of the ortho and para isomers was determined by titrating the resulting solution for inorganic bromide ion.



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(1) Presented at the Eleventh National Organic Chemistry Symposium, June, 1949, at Madison, Wisconsin.

(2) Atomic Energy Commission Predoctoral Fellow; American Cyanamid Co., Stamford, Conn.

(3) See, for example, G. W. Wheland, "The Theory of Resonance," John Wiley & Sons, Inc., New York, N. Y., 1944, pp. 256–272.

(4) E. Mameli, *Gazz. chim. ital.*, **52I**, 352 (1922); O. Dimroth, *Ber.*, **35**, 2032 (1902).

(5) S. Coffey, *J. Chem. Soc.*, **127**, 1029 (1925).

(6) J. Jürgens, *Rec. trav. chim.*, **45**, 61 (1926); S. Coffey, *J. Chem. Soc.*, 3215 (1926).

(7) O. Dimroth, *Ann.*, **446**, 148 (1925).

(8) F. Westheimer, E. Segel and R. Schramm, THIS JOURNAL, **69**, 773 (1947).

(9) R. Schramm, W. Klapproth and F. Westheimer, *J. Phys. Chem.*, in press.

(10) For a good review, see R. Gillespie and D. Millen, *Quart. Rev.*, **2**, 227 (1948).

(11) M. Kharasch and L. Chalkley, Jr., THIS JOURNAL, **43**, 607 (1921).

The analysis of the mixture of isomers obtained on mercurating toluene proved much more difficult. The mercurated toluenes were converted smoothly to bromotoluenes, but it was not possible to separate these isomers by distillation. They can be oxidized to the corresponding bromobenzoic acids, but the separation[5] of these compounds is arduous and incomplete. Recourse was therefore made to analysis with radiobromine. The mercurated toluenes were converted, with radiobromine, to radioactive bromotoluenes. To each of three samples of this mixture, a quantity of one pure isomer of non-radioactive bromotoluene was added as carrier, and the isomers separately oxidized to the corresponding bromobenzoic acids. These acids were crystallized to radiochemical purity; the ratio of the radioactivities of these samples gave the ratio of the amounts of individual isomers formed during mercuration. The analysis as conducted was independent of the yields obtained in the oxidation and purification steps of the process, and was dependent only on the purity of the samples finally obtained.

$$C_6H_5CH_3 + Hg^{++} \xrightarrow{HClO_4} C_6H_4(CH_3)Hg^+ + H^+ \quad (3)$$

$$C_6H_4(CH_3)Hg^+ + NaBr \longrightarrow C_6H_4(CH_3)HgBr + Na^+ \quad (4)$$

$$C_6H_4(CH_3)HgBr + Br{-}Br^* \longrightarrow C_6H_4(CH_3)Br^* + HgBr_2 \quad (5)$$

$$C_6H_4(CH_3)Br^* \xrightarrow{KMnO_4} Br^*C_6H_4CO_2H \quad (6)$$

Results and Discussion

Mercuration of Nitrobenzene.—The results obtained on mercurating nitrobenzene under a variety of conditions are shown in Table I.

TABLE I

ORIENTATION EFFECTS IN THE MERCURATION OF NITROBENZENE

Sample	Conditions	% of isomers found $o + p$	m
I	$Hg(ClO_4)_2$ in 60% $HClO_4$ at 23°	11	89
II	$Hg(ClO_4)_2$ in 40% $HClO_4$ at 95°	37	63
III	$Hg(OAc)_2$ in nitrobenzene at 95°	52	48
IV	$Hg(OAc)_2$ in nitrobenzene at 150°	57	43

The 89% meta orientation obtained in mercuration at 23° (sample I) compares favorably with the 91% meta orientation observed in the nitration[12] of nitrobenzene at 30°. It is apparent that, with an ionic reagent and at low temperatures, mercuration of nitrobenzene obeys the usual rules for electrophilic substitution.

By way of contrast, the classical method of mercuration (mercuration with mercuric acetate at the high temperatures required to get reasonably fast reaction) gives only slightly more than the 40% of meta which must be expected, in the absence of any orienting effects, on statistical grounds. At 95°, however, the two methods give more nearly similar results, although at this temperature, too, the ionic reagent shows stronger orientation effects. Incidentally, the fact that the ionic reagent not only shows greater orienting effects but also reacts much faster than does un-ionized $Hg(OAc)_2$ is consistent with the theory of electrophilic substitution.

Mercuration of Toluene.—The analysis of the products in the mercuration of toluene is complicated by the fact that it is impossible under certain experimental conditions to avoid rather extensive polymercuration. In order to minimize this side-reaction, mercuration in perchloric acid solution could be allowed to proceed only 1–2% to completion; the small samples obtained under these conditions could be accurately analyzed by our radiochemical technique. Very crude and preliminary results on the further mercuration of the *o*-, *m*- and *p*-mercurated toluenes suggested that their rates of further mercuration were not too greatly different; it then follows that the small amount of polymercuration here found will not invalidate the analyses. The results are shown in Table II.

TABLE II

ORIENTATION EFFECTS IN THE MERCURATION OF TOLUENE

Sample	Conditions	Per cent. of isomers found ortho	meta	para	Percentage of dimercuration
I	$Hg(ClO_4)_2$ in 40% $HClO_4$ at 25°	19	7	74	5
II	$Hg(ClO_4)_2$ in 20% $HClO_4$ at 85°	27	13	60	11
III	$Hg(OAc)_2$ in toluene at 110°	41	21	37	6
IV	$Hg(OAc)_2$ in HOAc plus $HClO_4$ at 25°	17	6	77	5
V	$Hg(OAc)_2$ in toluene at 110° (Coffey[5])	43	13	44	*ca.* 15

The 6–7% meta isomer obtained under ionic conditions at 25° is at least in fair agreement with the 4.4% meta isomer obtained on nitration of toluene[13] at 30°. Coffey's earlier results agree with ours with respect to the large quantity of ortho isomer formed; considering the difficulty and uncertainty of his analytical method, the discrepancy with respect to the quantity of meta isomer is understandable.

Again, as in the mercuration of nitrobenzene, the orientation is less sharply defined at higher temperatures. Qualitatively, this effect can be anticipated,[14] since orientation in electrophilic substitution should approach the statistical distribution (40% ortho, 40% meta and 20% para) at high temperatures, provided only that, for substitution in the various ring positions, the entropies of activation are equal. The lack of clearly defined orientation effects on mercuration with mercuric acetate is in part due to the fact that, to obtain reasonable rates, the reaction must be carried out at elevated temperatures. The data show, however, that the orientation

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[12] A. Holleman and B. de Bruyn, *Rec. trav. chim.*, **19**, 79 (1900).

[13] A. Holleman, J. Vermeulen and W. DeMooy, *Rec. trav. chim.* **33**, 1 (1914).

[14] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 125.

effects are more clearly defined with mercuric perchlorate even at elevated temperatures. The ratio of isomers obtained by high temperature reaction with mercuric acetate is clearly and appreciably different from the other data.

Experimental

Reagents.—Nitrobenzene and piperidine were distilled before use. Eastman Kodak Co. bromotoluenes were distilled through an 18″ Podbielniak column; Eastman Kodak Co. bromobenzoic acids were recrystallized to raise their melting points to the literature values. Eastman 2,5-dibromotoluene was used directly; 3,5-dibromotoluene was prepared by a slight modification of the method for 1,3,5-tribromobenzene.[15] Merck Reagent Grade toluene was washed with five successive portions of concentrated sulfuric acid, washed with alkali, dried and fractionated through a 36″ Podbielniak column. This purification proved necessary to remove a trace of a very reactive impurity which contaminated the mercuration samples taken at short time intervals. Two large samples of radioactive potassium bromide (Br^{82}, half-life 34 hours) were obtained from the Clinton Laboratory, Oak Ridge, Tennessee; smaller quantities of radiobromine, used to test the purification procedures, were obtained on several occasions by bombardment of sodium bromate solution in the 35″ cyclotron of the University of Chicago.[16]

All other chemicals were A. R. or reagent grade, and were used without further purification.

Mercuration of Nitrobenzene.—(I) To 250 cc. of 60% perchloric acid in a 500-cc. flask, 5.42 g. of mercuric oxide and 10 cc. of nitrobenzene were added. The reaction mixture was shaken every few hours and allowed to react at room temperature (23°) for 8 to 10 days. The product was isolated by pouring the mixture into twice its volume of ice-water, and precipitating the product with aqueous sodium chloride, as a mixture of nitrophenylmercuric chlorides. The precipitate was washed with water, 50% alcohol, ether and petroleum ether, and then dried; it weighed 7.9–8.7 g., melting range 215–221°.

(II) The experiment at 95° was similar, except that 40% perchloric acid was used, and the reaction time was 11 hours.

(III and IV) Nitrobenzene was mercurated with mercuric acetate according to Dimroth.[7] The reaction at 95° was allowed to proceed for 44 hours, that at 150° for 2.5 hours.

Analysis.—The conversion of the nitrophenylmercuric chlorides to bromonitrobenzenes was carried out by Dimroth's method, but his analysis with hydrazine was abandoned in favor of a modification by Campbell, Anderson and Gilmore.[17] Our investigations showed that 44 hours were required to get complete reaction of piperidine with *p*-nitrobromobenzene at 55°; under these conditions the meta isomer had reacted less than 0.3%.

Mercuration of Toluene.—Samples of mercurated toluenes were prepared as follows: (I) A solution of 108 g. of mercuric oxide in 500 cc. of 40% perchloric acid was thermostated at 25° and stirred vigorously. An excess of toluene (50 cc.) was added; five minutes later the reaction was stopped by the addition, with vigorous stirring, of a solution of 210 g. of sodium bromide (to convert the mercuric salt to $HgBr_4^=$ and to precipitate the tolyl mercuric bromides) and 200 g. of sodium acetate (to reduce the acidity of the solution) in 400 cc. of water. Since the solubility of the tolyl mercuric bromides in concentrated sodium bromide solution proved to be less than 0.01 mg./cc., no significant loss or enrichment of isomers occurred at this step. The mixture of tolyl mercuric bromides was filtered, washed with sodium bromide solution and then with water and dried in vacuum; yield 2.2 g., or 1.2% based on the HgO; melting range 190–210°.

(II) For the high temperature mercuration in perchloric acid, an acid strength of 20% was chosen in order to obtain a reasonable reaction rate. The method was similar to that used at 25°, except that the reaction was carried out for one minute at 85°. The yield from 22.7 g. of HgO in 150 cc. of 20% perchloric acid was 1.9 g., or 3.4% based on the HgO; melting range, 173–222°.

(III) The "classical" mercuration was carried out by refluxing a solution of 40 g. of mercuric acetate in 200 cc. of toluene for 1.5 hours. The reaction mixture was cooled and filtered to remove excess mercuric acetate and polymercurated material; the precipitate was washed with acetic acid and toluene to remove monomercurated product. (The amount of polymercurated material in this precipitate was determined later.) The combined filtrate and washings were transferred to a flask containing 300 cc. of water, and the toluene removed under vacuum. A solution of sodium bromide was added to precipitate the tolyl mercuric bromides; yield 11.9 g. or 25.6% based on the mercuric acetate; melting range 135–160°.

(IV) The mercuration in acetic acid was carried out as follows: 8 g. of mercuric acetate, 2.14 cc. of 70% perchloric acid and 26.6 cc. of toluene were added to 225 cc. of glacial acetic acid. After ninety minutes at 25°, the reaction was stopped by diluting the mixture with water. The excess toluene was removed under vacuum, and a solution of sodium chloride added. The tolylmercuric chlorides were filtered off, washed, and dried in vacuum; yield 6.4 g., or 78% based on the mercuric acetate; melting range, 185–210°.

Analysis.—The irradiated potassium bromide (0.9 g.) obtained from Oak Ridge was dissolved in 50 cc. of water and kept inside a thick lead cage. Portions of the solution were withdrawn as required, and shaken with solution of bromine in chloroform.[18] Since the amount of bromine was much greater than the amount of bromide, most of the radioactivity was extracted into the bromine layer.

About 0.5 g. of the mercurial was stirred with 50 cc. of chloroform. The radioactive bromine was added in small portions until the brown color of bromine persisted; the mixture was stirred an additional two hours to assure complete reaction. The excess bromine was then converted to bromide with sodium bisulfite solution, and the mercuric bromide formed (equation 5) was extracted with aqueous sodium bromide solution. The chloroform solution was washed, and then divided into three 100-cc. portions. Ten grams of each of the three pure isomeric bromotoluenes had previously been weighed out in three separate flasks. One of the 100-cc. portions of the labeled tracer mixture (equation 5) was added to each flask; the weight of tracer was thus small compared to the weight of carrier. The chloroform was distilled from each sample through a short column, and the last traces of this solvent removed by steam distillation with added water. The residue was oxidized with permanganate and alkali.[19]

The following procedures for the purification of the bromobenzoic acids were carried out concurrently over a period of two days.

Ortho.—The manganese dioxide was removed by filtration, and the solution evaporated to 400 cc. The hot solution was acidified with 6 *N* hydrochloric acid and treated twice with 1-g. portions of charcoal. It was then extracted with ether. The ether was evaporated and the residue recrystallized twice from a 5 to 1 mixture of carbon tetrachloride and absolute alcohol. The recrystallizations were purposely "wasteful"; only 50–75% of the material was recovered each time. The product from the second recrystallization was weighed, and accurately diluted with enough pure inactive *o*-bromobenzoic acid to make a total of about 3 g. The isotopically diluted acid was then recrystallized from the carbon tetrachloride–ethanol mixture, dried and counted; the process was repeated until further recrystallization did not change the counting rate.

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(15) G. Coleman and W. Talbot, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 592.

(16) This cyclotron was operated under Navy Contract N-6-ori-20, Task Order III.

(17) N. Campbell, W. Anderson and J. Gilmore, *J. Chem. Soc.*, 446 (1940).

(18) R. Dodson and R. Fowler, THIS JOURNAL, **61**, 1215 (1939).

(19) L. Bigelow, *ibid.*, **44**, 2010 (1922).

TABLE III

ANALYSES OF ISOMERIC MIXTURES FROM MERCURATION OF TOLUENE

Sample	Carrier isomer	Time counted, min.	Total no. of counts	Back-ground, c./m.	% Error at 90% confidence level	Diln. corrn.	Decay corrn.	C./m. over background corrd.	Rel. percentages
$Hg(ClO_4)_2$ in 40% $HClO_4$ at 25°	Ortho	38	14,572	23.0	1.4	2.118	...	763.6	19.0 ± 0.3
	Meta	195	13,819		1.4	5.140	1.136	279.7	7.0 ± 0.1
	Para	27	24,073		1.1	2.884	1.185	2968.5	74.0 ± 0.8
$Hg(ClO_4)_2$ in 20% $HClO_4$ at 85°	Ortho	75	13,784	23.2	1.4	3.250	1.036	540.7	27.3 ± 0.4
	Meta	110	11,244		1.6	3.169	...	250.5	12.6 ± 0.2
	Para	10	11,909		1.5	..	1.021	1191.7	60.1 ± 0.9
Toluene and $Hg(OAc)_2$ at 110° ("classical")	Ortho	15	13,124	24.7	1.5	1.987	1.010	1706.2	41.4 ± 0.6
	Meta	40	12,177		1.5	3.150	...	881.0	21.4 ± 0.3
	Para	10	11,221		1.6	1.376	1.014	1531.2	37.2 ± 0.6
$Hg(OAc)_2$ and $HClO_4$ in HOAc at 25°	Ortho	20	14,072	24.9	1.4	2.691	...	1826.4	17.3 ± 0.2
	Meta	140	13,140		1.5	9.157	1.035	653.9	6.2 ± 0.1
	Para	20	23,478		1.2	6.977	1.007	8072.8	76.5 ± 0.9

TABLE IV

ANALYSIS FOR DIMERCURATION

Sample	Carrier bromotoluene	Time counted, min.	Total no. of counts	Back-ground, c./m.	% Error at 90% confidence level	Diln. corrn	Decay corrn.	C./m. over background corrd.	Rel. mole %
40% $HClO_4$ at 25°	Mono	8	14,563	24.0	1.4	...	...	1796.4	94.9 ± 1.3
	Di	62	10,401		1.6	1.335	1.010	96.9	5.1 ± 0.1
20% $HClO_4$ at 85°	Mono	4	19,274	24.0	1.2	...	...	4794.5	89.0 ± 1.1
	Di	38	34,501		0.9	1.337	1.008	595.6	11.0 ± 0.1
"Classical" method	Mono	35	10,992	23.5	1.6	...	...	290.6	95.0 ± 1.5
	Di	230	10,483		1.6	1.332	1.049	15.4	5.0 ± 0.1[a]
HOAc + $HClO_4$ at 25°	Mono	2	15,648	23.5	1.3	1.008	1.038	8161.7	95.4 ± 1.2
	Di	47	37,934		0.9	...	...	391.8	4.6 ± 0.0

[a] Adding the 0.5 mole % found in the precipitate from the reaction mixture makes a total of 5.5 mole % dimercuration.

Meta.—The manganese dioxide was filtered from the oxidation mixture, and the filtrate acidified and cooled. The dried, impure *m*-bromobenzoic acid was dissolved in 600 cc. of hot 50% ethanol, and 10 g. of inactive *p*-bromobenzoic acid added as a "hold-back" carrier. The solution was allowed to cool slowly, and the precipitated para acid removed by filtration. The alcoholic solution was then boiled down to 300 cc., barium hydroxide added, and the resulting barium salt[5] recrystallized from water. The acid recovered from the barium salt was recrystallized from 50% methanol. One-half to 1.5 g. of meta acid was so obtained, and was accurately diluted with inactive meta acid to about 4 g.; this acid was treated twice in hot 20% ethanol solution with 1-g. portions of norite. The solution was then cooled and the acid crystallized, recrystallized from 25% methanol, and dried and counted. This complex procedure for the meta acid was necessary because the para acid showed a strong tendency to coprecipitate with the meta acid, especially when there was only a small amount of the former present. There may be mixed crystal formation, although, if this is the fact, it is restricted to a small part of the composition range of mixtures[20] of meta and para acids.

Para.—The manganese dioxide was filtered from the oxidation mixture, the filtrate acidified and filtered hot. The para acid was twice recrystallized from 50% ethanol. Frequently the acid was so radioactive that it had to be diluted to minimize counter coincidence losses.

The counting was performed with a thin-walled (2.3 mg./cm.^{2}) end-window Geiger–Muller tube; the "scaler" was a Nuclear Instrument Development Laboratories Model 163. The samples were mounted in aluminum discs drilled with holes 3.0 mm. deep and 10 mm. in diameter. The samples to be counted were all finely ground and about 270 mg. in weight; they were packed smoothly to the top of the holes. This uniform weight and packing was necessary because of the gamma radiation[21] which accompanies the beta radiation of Br^{82}. All samples were counted long enough to register at least 10,000 counts; the counter was standardized at regular intervals with a U_{x1} standard.

In each analysis, a decay correction was applied to two of the three analyses, correcting these to the activity which would have been observed had all the samples been counted simultaneously.

Determination of the Amount of Polymercuration.—The procedure was the same as that outlined for the preparation of labeled bromotoluenes except that the bromine was made by the Szilard–Chalmers reaction,[22] using the 35″ cyclotron at the University of Chicago as a neutron source. The carrier usually consisted of a mixture of 15 g. of *p*-bromotoluene, 10 g. of 2,5-dibromotoluene and 10 g. of 3,5-dibromotoluene. The mono- and dibrominated fractions were separated by distillation through an 18″ Podbielniak column at about 50 mm. pressure. Since the monobromotoluenes all boil within 2° of the para isomer, and since all the dibromotoluenes boil between the two isomers chosen as carriers, there should be little or no fractionation of isomers during the distillation procedure. Samples of the mono- and dibrominated products were then counted.

The amount of polymercuration in the precipitate recovered from the "classical" mercuration procedure was also determined. The mercuric bromide was removed with aqueous sodium bromide, and the residue dried and

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(20) H. Lettre, H. Barnbeck, W. Fuhst and F. Hardt, *Ber.*, **70**, 1410 (1937).

(21) A. Roberts, J. Downing and M. Deutsch, *Phys. Rev.*, **60**, 544 (1941).

(22) L. Szilard and T. Chalmers, *Nature*, **134**, 462 (1934); W. Libby, THIS JOURNAL, **62**, 1930 (1940).

weighed. The amount of polymercuration so determined was added to that found by the carrier technique.

Acknowledgments.—The authors gratefully acknowledge the Fellowship granted to one of us (W. K.) by the Atomic Energy Commission, and the help and coöperation of Dr. Gerhart Groetzinger of the Institute for Nuclear Studies, who bombarded the sodium bromate solution from which some of the needed Br^{82} was obtained.

Summary

1. Both toluene and nitrobenzene were mercurated (a) with mercuric acetate, and (b) with mercuric perchlorate in perchloric acid solution.

2. The amounts of ortho and para and of meta isomers thus formed were determined in each case. The analytical method for the tolyl mercuric salts depended upon converting these compounds to bromotoluenes, and analyzing these by a tracer technique requiring Br^{82}.

3. It was found that mercuration with mercuric perchlorate in perchloric acid solution gave the pronounced orientation effects typical of electrophilic substitution; mercuration with unionized mercuric acetate showed much less strongly marked orientation effects.

CHICAGO, ILLINOIS RECEIVED MARCH 18, 1950

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIV., POLYMER CORPORATION LTD.]

The Decomposition of Cumene Hydroperoxide by Ferrous Iron in the Presence of Oxygen[1]

BY J. W. L. FORDHAM AND H. LEVERNE WILLIAMS

In most low temperature free radical initiated emulsion polymerization recipes the initiating free radicals are formed by the reaction between cumene hydroperoxide (CHP, $C_6H_5C(CH_3)_2OOH$) and complexed ferrous iron. In order to obtain information on the rate of production of these free radicals under various conditions a study of the decomposition of CHP was undertaken. In a previous publication[2] it was shown that in the vicinity of 100° the decomposition of CHP in a styrene solution may be described by two simultaneous reactions, a unimolecular fission presumably at the O—O bond producing two radicals per molecule ($k = 2.7 \times 10^{12}e^{-30,400/RT}$ sec.$^{-1}$). and a radical induced decomposition having no effect on the number of radicals in the system ($k = 1.00 \times 10^5e^{-6,500/RT}$ l. mole^{-1} sec.$^{-1}$). The present paper deals with the decomposition of CHP in an acidic dilute aqueous solution at lower temperatures in the presence of ferrous iron and oxygen with particular emphasis on the rate constant of the primary radical producing reaction and as an intermediate step to the study of the decomposition in alkaline medium in the presence of complexed iron. The study was carried out in the presence of oxygen rather than its absence because of the experimental difficulty of removing completely from very dilute solutions the effect of oxygen traces. Very little has been reported on this although Kolthoff and Medalia[3] obtained an approximate value of 27 l. mole^{-1} sec.$^{-1}$ at 27° for the rate constant of the primary radical producing reaction. Baxendale, Evans and Park[4] in a study of the analogous reaction between hydrogen peroxide and ferrous iron found that the rate constant of the reaction is given by $k = 1.78 \times 10^9e^{-10,100/RT}$ l. mole^{-1} sec.$^{-1}$.

Stoichiometric Ratios.—Publications[4,5,6] indicate that in dilute aqueous solutions of hydrogen peroxide and ferrous iron the ratio of ferrous iron oxidized to peroxide consumed in an acidic medium is two to one whether the reaction takes place in the absence or presence of oxygen. This fact supports the mechanism proposed for dilute solutions of low *p*H,[4] *i.e.*

$$Fe^{++} + HO_2H \longrightarrow Fe^{+++} + OH^- + HO\cdot$$
$$Fe^{++} + HO\cdot \longrightarrow Fe^{+++} + OH^-$$

However, in the CHP–ferrous iron reaction under similar conditions, the ratio is approximately one to one in the absence of oxygen and varies from slightly less than two to more than four to one depending upon the initial concentration of CHP and ferrous iron in the presence of oxygen.[3] The authors have also found the ratios are considerably greater than two to one in the presence of oxygen. The stoichiometry of the reaction in an alkaline medium could not be investigated in the presence of oxygen because of the rapid oxidation of ferrous iron in the absence of hydroperoxide. The results are in Tables I and II.

From these results it is evident that at a *p*H from 1 to 4 an increase in the initial ratio of ferrous iron to CHP, a decrease in the *p*H of the solution, or a decrease in the initial CHP con-

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[1] Presented at the Detroit Meeting, Division of Physical and Inorganic Chemistry, American Chemical Society, April, 1950.

[2] J. W. L. Fordham and H. L. Williams, *Can. J. Research*, **27B**, 943 (1949).

[3] I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3789 (1949).

[4] J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

[5] I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777 (1949).

[6] I. M. Kolthoff and A. I. Medalia, *ibid.*, **71**, 3784 (1949).