TABLE XVII

DECOMPOSITION OF C

$[C] = 9.23 \times 10^{-3}$ mole/l., $[CH_3COOH] = 4.55 \times 10^{-2}$ mole/l., $[AgNO_3] = 2.28 \times 10^{-2}$ mole/l., $t = 20°$

T (sec.)	% C dec.	$k \times 10^4$
510	8.6	1.68
720	11.5	1.69
1200	17.2	1.57
1400	22.3	1.82

The rate constants determined at various temperatures are listed in Table XVIII.

TABLE XVIII

$[C] = 9.23 \times 10^{-3}$ mole/l., $[CH_3COOH] = 4.55 \times 10^{-2}$ mole/l., $[AgNO_3] = 2.28 \times 10^{-2}$ mole/l., $E = 15{,}000$ cal./mole, $C = 1.52 \times 10^7$, $\Delta S^* = -2.77$ cal./deg., 25°.

Temp., °C.	$k \times 10^4$
20	1.6
23	1.8
25	2.5
30	3.0

MEGURO, TOKYO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Kinetics of Ozonization of Polyalkylbenzenes

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A spectrophotometric method has been employed in studying the kinetics of the reactions of a series of polyalkylbenzenes with ozone in carbon tetrachloride and in acetic acid at 25°. Rate constants have been calculated on the assumption that the reactions are first order in ozone and in aromatic hydrocarbon and that three molecules of ozone are consumed per mole of aromatic substance. For reaction in a particular solvent the logarithms of the constants for the polymethylbenzenes increase linearly with the number of methyl substituents on the aromatic nucleus. The rate constants for the polyethyl- and polyisopropylbenzenes are similar in magnitude to those for the polymethylbenzenes with the exception of that for hexaethylbenzene. The logarithms of rate constants for this compound and for *t*-butyl substituted benzenes fall far short of the line which best accommodates the data for their methyl analogs, a fact which is explained on steric grounds. The products of ozonization of the aromatic hydrocarbons at 25° are similar to those formed at much lower temperatures.

Because of the favorable electronic influences of alkyl substituents on π electron availability, the stabilities of donor–acceptor complexes of polymethylbenzenes with iodine and with iodine monochloride increase as the donor ring becomes more extensively alkylated.[1,2,3] With the exception that hexaethylbenzene is a very weak donor the polyethylbenzene–halogen complexes also become more stable as the number of ring substituents is increased. Presumably the six large alkyl groups in the hexaethylbenzene molecule inhibit the coördination of an acceptor by forming a protective screen about the electrons of the aromatic nucleus.

It may be anticipated, if the steric interpretation of its low donor strength is correct, that hexaethylbenzene will also be unusually resistant to attack by electrophilic reagents. Two such reagents which are appropriate for use in studying hexaalkylbenzenes are perbenzoic acid[4] and ozone.[5] It has been shown previously[4] that perbenzoic acid reacts somewhat less rapidly with hexaethylbenzene than with hexamethylbenzene in chloroform, although it oxidizes mesitylene and 1,3,5-triethylbenzene at comparable rates. The differences in reactivity of the two hexaalkylbenzenes are not, however, sufficiently large to support strongly the argument that the hexaethyl derivative is, for steric reasons, resistant to electrophilic attack.

In earlier investigations of the kinetics of ozonization of aromatic hydrocarbons in solution, the reaction mixtures were continuously saturated with ozone, and the concentrations of the benzene derivatives were relatively high initially.[5-7] Even at temperatures below 0° the more highly alkylated benzenes proved to be so reactive that they were susceptible only to qualitative investigation when this procedure was used. A spectrophotometric method for studying aromatic ozonization kinetics has now been developed which is applicable to solutions of the reactants at high dilution at room temperature. This method has been successfully applied in demonstrating that hexaethylbenzene is indeed much less reactive than hexamethylbenzene in both carbon tetrachloride and acetic acid. Ozonization rate constants for a large number of other alkyl substituted benzenes in these solvents also have been determined. In general the effects of alkyl substituents on alkylbenzene reactivity (with respect to ozone) are parallel to those encountered in investigating halogen complex stabilities.

Experimental

Materials.—With certain exceptions the sources and methods of purification of the alkylbenzenes already have been described.[3] Hemimellitene, pseudocumene and *t*-butylbenzene of purissima grade were obtained from the Aldrich Chemical Co. and were used without further treatment.

Acetic acid was purified for use as a solvent in rate work by the procedure of Orton and Bradfield.[8] It was established by spectrophotometric methods that ozone decomposed in this solution at the approximate rate of 8% per hour at 25°.

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[1] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952).

[2] R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

[3] N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

[4] L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 2545 (1955).

[5] J. P. Wibaut and F. L. J. Sixma, *Rec. trav. chim.*, **71**, 761 (1952).

[6] J. Van Dijk, *ibid.*, **67**, 945 (1948).

[7] F. L. J. Sixma, H. Boer and J. P. Wibaut, *ibid.*, **70**, 1005 (1951).

[8] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 960 (1924).

Eastman Organic Chemicals carbon tetrachloride (sulfur free) was subjected to further purification, since ozone was found to decompose to the extent of about 50% per hour in the untreated solvent. The carbon tetrachloride was ozonized for 30 minutes in a gas washing bottle at a flow rate of 17 l./hr. and an ozone delivery rate of 30 mmoles/hr. at room temperature. The dissolved ozone then was removed by flushing the contents of the gas washing bottle with dry nitrogen for several hours. The solvent which had been thus pretreated was used for rate work without further purification. It contained 1.2×10^{-4} mole/l. of reducible material (by iodometric analysis). When ozone was dissolved in the pretreated solvent, it decomposed at a rate of only 6% per hour. The reducible impurity was not removed on efficient fractionation. It could be destroyed by treatment of the carbon tetrachloride with aqueous potassium iodide followed by reduction of liberated iodine with sodium thiosulfate; however, the rate of ozone decomposition in solvent which had been so treated was again high.

Ozone was produced using a Welsbach Corporation model T-23 laboratory ozonizer. Oxygen was purified by a method described elsewhere[9] before it was introduced into the ozonizer. In some experiments a constant delivery rate of ozone was required. When the ozonizer was operated to provide 13.9 mmoles of ozone per hour, the relative deviation (as established by periodic analyses of the emerging gas) from the mean delivery rate was 1.5% over a one hour interval.

Kinetic Measurements.—Dilute solutions of ozone and the aromatic hydrocarbon (10^{-3} to 10^{-5} M) in the appropriate purified solvent were brought to the temperature at which the rate runs were conducted. A known volume of the ozone solution was added to a glass stoppered absorption cell, and the optical density then was measured (after equilibration to the housing temperature) to establish the ozone concentration. The cell housing temperature was controlled to ±0.1° at 25° and to ±0.2° at lower or higher temperatures. One ml. of the appropriate hydrocarbon solution was added to the absorption cell to initiate the reaction. In all cases the initial concentrations of reactants were chosen so that during the ozonization reaction only a negligible amount of ozone was lost through other processes not involving organic substances. Optical density readings, at some wave length in the 280–310 mμ region, were made at various times until the reaction terminated (as indicated by the constancy of optical density readings). In some instances the optical densities did not fall to a constant value but instead passed through a minimum value and then increased slowly. In such cases the minimum readings were selected as representing the termination of the primary ozonization reaction.

To establish the extinction coefficients of ozone in acetic acid and in carbon tetrachloride a sample of a freshly prepared ozone solution was taken by pipet. A portion of the pipet contents was used to rinse an absorption cell. A second portion was used to fill the cell for spectrum measurement, and the remainder was added to a tared 50-ml. glass stoppered flask containing aqueous potassium iodide. The flask was weighed again to determine the quantity of ozone solution added, and the contents then were titrated with standard aqueous sodium thiosulfate solution. In Table I are listed representative values of the ozone extinction coefficients, which were obtained in this way.

TABLE I

OZONE EXTINCTION COEFFICIENTS[a]

λ, mμ	270	280	290	300	310	320	350
$\epsilon(CCl_4)$	2530	1670	789	264	74	20	0.8
$\epsilon(HOAc)$	1790	1160	558	207	69	..	...

[a] Several check determinations of the extinction coefficients in both solvents were made. Average deviations from reported values were of the order of 1.5% for carbon tetrachloride and 3% for acetic acid.

The extinction coefficients of the pure aromatic hydrocarbons at the wave lengths used in rate experiments were determined, as required, by measurement of solutions of known concentrations.

The final optical densities (d_∞) of the rate runs in which the initial aromatic hydrocarbon concentration, $(ArH)_i$, was in stoichiometric excess of the initial concentration of ozone, $(O_3)_i$, were used to evaluate the extinction coefficients of the products (equations 1 and 2).

$$ArH + nO_3 \longrightarrow \text{Products (P)} \qquad (1)$$

For $(ArH)_i > (O_3)_i/n$

$$d_\infty/l = (O_3)_i\, \epsilon_P/n + [(ArH)_i - (O_3)_i/n]\epsilon_{ArH} \qquad (2)$$

The terms ϵ_P and ϵ_{ArH} represent the extinction coefficients of the product and the hydrocarbon, and l is the path length of the absorption cell.

The wave length was chosen so that the extinction coefficient of ozone was considerably larger than that of the hydrocarbon or the product. In all runs the optical density of the unreacted hydrocarbon (the second term on the right side of equation 2) was very small, so that values of ϵ_P/n were independent of the value of n. Typical values of ϵ_{O_3}, ϵ_{ArH} and ϵ_P/n are (a) for a run with benzene in acetic acid at 308 mμ, 87.7, 0.01 and 2.9, respectively, (b) for a run with mesitylene in carbon tetrachloride at 300 mμ, 264, 0.2 and 27, respectively.

At any time t during the course of a rate run the optical density d_t may be related to the composition of the solution by equation 3

$$d_t/l = [(ArH)_i - (O_3)_i/n + (O_3)_t/n]\epsilon_{ArH} + (O_3)_t\epsilon_{O_3} + [(O_3)_i - (O_3)_t]\epsilon_P/n \qquad (3)$$

The ozone concentration at any time during the run may be calculated from equation 4 which is derived from equations 1 and 2.

$$(O_3)_t = (d_t - d_\infty)/l[\epsilon_{O_3} - \epsilon_P/n + \epsilon_{ArH}/n] \qquad (4)$$

The evaluation of the ozone concentration from optical densities of the reaction mixtures is essentially independent of the value of n, since (as previously noted) the value of ϵ_P/n is independent of n and ϵ_{ArH}/n is very small compared to ϵ_{O_3}. It should be noted that the term ϵ_P/n probably encompasses several reaction products and is of no more than practical significance in the evaluation of rate constants.

The Stoichiometry of the Reaction. (A) As Established under the Conditions of the Rate Runs.—In attempting to establish the mole ratio of ozone to aromatic hydrocarbon consumed, a number of rate runs in which the ozone was in stoichiometric excess of the hydrocarbon were conducted. In runs with the less reactive hydrocarbons the ozone concentration at termination of reaction could not be ascertained with certainty because of the complication of a slow follow reaction of excess ozone (presumably with the initial reaction products). However, in the case of hexamethylbenzene in carbon tetrachloride the following reactions were sufficiently slow, relative to the hydrocarbon ozonization, so that the concentration of excess ozone could be calculated reliably from final optical density readings using equation 5

$$d_f/l = (O_3)_f\, \epsilon_{O_3} + [(O_3)_i - (O_3)_f]\epsilon_P/n \qquad (5)$$

The required values of ϵ_P/n were calculated from the final optical densities of runs in which excess hexamethylbenzene was present (see equation 2). The results of two separate runs are

(a) $(HMB)_i = 3.09 \times 10^{-5}$ M, $(O_3)_i = 20.1 \times 10^{-5}$ M, $(O_3)_f = 11.1 \times 10^{-5}$ M, $n = 2.9$; (b) $(HMB)_i = 6.40 \times 10^{-5}$ M, $(O_3)_i = 21.0 \times 10^{-5}$ M, $(O_3)_f = 2.4 \times 10^{-5}$ M, $n = 2.9$.

(B) **As Established** by **Ozone Absorption Experiments.**—To establish the value of n for aromatic hydrocarbon ozonization Sixma, Boer and Wibaut[5] gassed a solution of *o*-xylene in chloroform at −40° with ozone at a constant known flow rate. The unabsorbed ozone was trapped, and the quantity collected per unit time was determined periodically. The time at which aromatic material was completely removed from solution could be determined only approximately because a sharp drop in the rate of ozone absorption does not occur at this point when a relatively unreactive hydrocarbon is used. It was, however, estimated from the experimental data that about 3 moles of ozone was absorbed per mole of *o*-xylene initially present in solution.

In the present investigation a modification of these procedures was used in which ozone was passed, at a known input rate of the order of 15 mmoles/hr., through the solvent before the aromatic hydrocarbon was added. The flow rate was established by collecting ozone in a potassium iodide

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[9] L. I. Smith, F. L. Greenwood and O. Hudrlik, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 673

trap, which followed the reaction vessel in the gas train, and analyzing the trap contents iodometrically. A weighed quantity of aromatic hydrocarbon then was added to the solvent. The trap was recharged with fresh potassium iodide solution, and ozone addition was continued at the same flow rate. Less than the stoichiometric amount of ozone was added. The trap contents were then analyzed for unreacted ozone, and the solutions in the reaction vessel were analyzed for unreacted hydrocarbon.

In the case of hexamethylbenzene in carbon tetrachloride the unreacted hydrocarbon was recovered by using a silica-gel chromatograph column (12 cm. tall and 2 cm. in diameter). Carbon tetrachloride product solutions were added directly to the column, and elution was accomplished with 100 ml. of carbon tetrachloride, 100 ml. of 1% 1-butanol (by volume) in carbon tetrachloride and 10% 1-butanol in carbon tetrachloride. The unreacted hydrocarbon, which appeared mainly in the first 100 ml. of effluent, was recovered by evaporation of the solvent and weighed, m.p. 163–166°. The recovery of hydrocarbon, as based on a control test with a solution of 0.250 g. of hexamethylbenzene in 25 ml. of carbon tetrachloride, was of the order of 98%.

When acetic acid was used as the solvent, the ozonized solution was poured into a large volume of water, and the hydrocarbon was extracted with ether. The residue remaining after evaporation of the ether phase was dissolved in carbon tetrachloride and the hexamethylbenzene was isolated by chromatography as described in the preceding paragraph. The recovery was 95% as established by a control experiment.

When mesitylene solutions were subjected to ozonization, the unreacted hydrocarbon was determined by gas–liquid chromatography using *p*-xylene as a marker.[10] Chromatograms for known mixtures of the two hydrocarbons on a column of polyethylene glycol-400 (Union Carbide Chemical Co.) absorbed on firebrick (Johns Manville Insulation Brick C-22 screened to −40 + 60 mesh) were obtained at a column temperature of 100° using helium as the carrier gas and a Gow Mac conductivity cell in the detector system. A calibration curve which compared the relative amounts of the two hydrocarbons to the relative areas (peak height times width at half height) of the chromatogram peaks was prepared for use in the analysis of unknowns.

In a typical analysis on a solution of 3.00 ml. of mesitylene in 100 ml. of carbon tetrachloride which had been treated with less than the stoichiometric amount of ozone, 10 ml. of methanol was added first to dissolve flocculent material which had formed. Then 4.00 ml. of *p*-xylene was added, and a 60 microliter sample of the resultant solution was analyzed on the chromatograph column. Much the same procedure was followed when acetic acid was used as the solvent. Analytical results on known mixtures were reproducible to within 1%.

When benzene solutions in carbon tetrachloride were ozonized, a Dry Ice trap was inserted between the reaction vessel and the potassium iodide absorber to collect any benzene which was entrained in the gas stream. After ozonization the contents of the reaction vessel and the Dry Ice trap were combined and treated with a small amount of ethanol to dissolve any precipitate which appeared. A known quantity of toluene was added as a marker, and the solution was analyzed for unreacted benzene by gas–liquid chromatography using techniques similar to those employed for mesitylene solutions. In a control experiment the above operations were repeated using an oxygen rather than an ozone stream to gas the benzene solution; 99% of the original benzene was accounted for by chromatographic analysis.

The experimental values for *n* as found through recovering untreated aromatic hydrocarbon from solutions which had absorbed less than the stoichiometric amount of ozone are given in Table II. It is surprising that *n* values of even less than 2 have been obtained by this procedure for the reaction of mesitylene in acetic acid and of hexamethylbenzene in both carbon tetrachloride and in acetic acid. It is possible that in the ozonization of these highly reactive hydrocarbons the differences in rate constants for the three reactions

$$\mathrm{ArH} \xrightarrow[\text{(I)}]{\mathrm{O_3}} \mathrm{ArH{\cdot}O_3} \xrightarrow[\text{(II)}]{\mathrm{O_3}} \mathrm{ArH{\cdot}2O_3} \xrightarrow[\text{(III)}]{\mathrm{O_3}} \mathrm{ArH{\cdot}3O_3}$$

may not be as extreme as for the less reactive alkylbenzenes. Thus in the initial stages of ozonization, when the hydrocarbon concentration is high relative to the concentrations of $\mathrm{ArH{\cdot}O_3}$ and $\mathrm{ArH{\cdot}2O_3}$, the assumption that reactions II and III are very rapid as compared to reaction I may not be valid. It is particularly surprising that *n* values of less than 3 have been observed for benzene, since this hydrocarbon should be much less reactive than its products of reaction with one and two moles of ozone.

TABLE II

THE OZONE–AROMATIC HYDROCARBON MOLE RATIO[a]

Aromatic hydrocarbon, mmole Initial	Aromatic hydrocarbon, mmole Recovered	O_3 absorbed, mmole	Solvent	$\frac{\text{Moles } O_3}{\text{moles ArH}} = n$
		Benzene		
55.6	50.6	10.8	CCl_4	2.16
22.2	18.8	7.7	CCl_4	2.25
		Mesitylene		
35.8	26.6	21.1	CCl_4	2.30
21.4	14.2	17.2	CCl_4	2.39
21.4	16.3	14.6	CCl_4	2.86
21.4	11.3	17.2	HOAc	1.70
35.8	25.9	16.6	HOAc	1.68
		Hexamethylbenzene		
18.5	7.8	18.9	CCl_4	1.77
18.5	14.7	6.3	CCl_4	1.65
9.25	6.41	4.6	HOAc	1.61
9.25	1.87	14.5	HOAc	1.97

[a] The volume of solvent was 100 ml.

Ozonization Products. (A) From Hexaethylbenzene in Carbon Tetrachloride.—A total of 13.9 mmoles of ozone was absorbed in a solution of 1.50 g. (6.09 mmoles) of hexaethylbenzene in 100 ml. of carbon tetrachloride. The techniques for adding and measuring ozone are described above. A sample of the product solution was removed for analysis for active oxygen containing compounds. The remaining solution was added to 25 ml. of an aqueous solution of 8.2 g. of hydroxylamine sulfate and 14 g. of potassium carbonate. After the mixture was stirred overnight, the precipitated material was collected and washed with ether. The aqueous phase of the filtrate was subjected to liquid–liquid extraction with ether for 24 hr. The combined ether extracts were concentrated to dryness. The crude bipropionyl dioxime thus obtained was purified by sublimation (130 mg. was recovered) and recrystallization from aqueous ethanol; m.p. 190–192° (lit.[11] m.p. 185°). On treatment of the derivative with nickel acetate the characteristic[12] red-orange complex formed.

The aqueous phase remaining from the liquid–liquid extraction was adjusted to *p*H 2 with sulfuric acid and distilled under reduced pressure. The distillate, as determined by titration with standard base, contained 4.5 meq. of propionic acid. This was identified by conversion[13] to *p*-phenylphenacyl propionate of m.p. 101–102° (after recrystallization from ethanol). The melting point was not depressed when the product was mixed with an authentic sample.

A second sample of hexaethylbenzene was ozonized in carbon tetrachloride, and the product solution was heated and stirred for 0.5 hr. with an aqueous solution of sodium acetate, phenylhydrazine hydrochloride and sodium metabisulfite. On concentration of the solution, yellow crystals of bipropionyl osazone separated. The melting point, after recrystallization from aqueous ethanol, was 159–161° (lit.[14] m.p. 161°).

Anal. Calcd. for $C_{18}H_{22}N_4$: C, 73.40; H, 7.53. Found: C, 73.17; H, 7.45.

(B) **From Hexamethylbenzene in Carbon Tetrachloride.**—A solution of hexamethylbenzene in carbon tetrachloride

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(10) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publ. Corp., New York, N. Y., 1957, p. 32.

(11) G. Ponzio, *J. prakt. Chem.*, **63**, 367 (1901).

(12) L. Chugaev, *Ber.*, **40**, 186 (1907).

(13) N. L. Drake and J. Bronitsky, THIS JOURNAL, **52**, 3715 (1930).

(14) I. Heilbron, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1953, p. 438.

was gassed with ozone until the ratio of moles of ozone absorbed to initial moles of hydrocarbon was 2.7. Biacetyl was recovered as its dioxime (m.p. and mixed m.p. with an authentic sample, 240–241°) by the same procedure as described in section (A) for the preparation of bipropionyl dioxime. The aqueous phase remaining from the preparation of the derivative was analyzed for acetic acid by the techniques described in section (A) for the detection of propionic acid. The acid was identified by conversion to *p*-phenylphenacyl acetate, m.p. and mixed m.p. with an authentic sample, 107–108°.

(C) From Mesitylene in Carbon Tetrachloride.—In experiments similar to those described in sections (A) and (B) methylglyoxal was recovered from the hydrolysate of the products of ozonization of mesitylene in carbon tetrachloride. The crude dioxime was purified by sublimation and recrystallization from benzene, m.p. 151–153°. The melting point previously has been reported to range from 150–165°.[15]

Anal. Calcd. for $C_3H_6O_2N_2$: C, 35.28; H, 5.92; N, 27.44. Found: C, 35.49; H, 6.03; N, 27.20.

The aqueous phase remaining from the preparation of the dioxime was acidified with sulfuric acid and distilled under reduced pressure. The distillate was titrated with standard base to determine its organic acid content, and the resultant solution was treated with *p*-phenylphenacyl bromide.

From the precipitate which formed *p*-phenylphenacyl acetate was recovered by a chromatographic procedure.[16]

(D) Products Detected under Non-hydrolytic Conditions.—A solution of 1.00 g. (6.2 mmoles) of hexamethylbenzene in 10 ml. of acetic acid was treated with excess (60 mmoles) ozone. The solution then was subjected to gas–liquid chromatography using a polyethylene glycol-400 column. The first emergent fraction was trapped at liquid air temperature. It was characterized as carbon dioxide by mass spectrometry by Professor R. K. Brinton, to whom the authors are indebted. A later fraction was identified as biacetyl through comparison of its retention time with that of a known sample.

A solution of 1.7 g. (15 mmoles) of mesitylene in 10 ml. of carbon tetrachloride was treated with 21 mmoles of ozone. The resultant solution was subjected to gas–liquid chromatography using a dinonyl phthalate column. Only one fraction, acetic acid, could be identified.

Solutions of hexamethylbenzene in carbon tetrachloride or acetic acid were found to develop the characteristic visible absorption peak of biacetyl (*ca.* 420 mμ) on ozonization. Using the extinction coefficients of the diketone, as determined by measuring its spectrum in the pure solvents, the biacetyl content of solutions of the hydrocarbons, to which less than the stoichiometric amount of ozone had been added, was determined by spectrophotometric methods.

(E) Analysis for Active Oxygen Containing Compounds.—Samples (1–3 ml.) of the various product solutions were analyzed for active oxygen containing compounds by essentially the same method used by Warnell and Shriner.[17] The samples were treated with an acetic acid solution of potassium iodide and hydrochloric acid. The mixtures were heated for ten minutes at 60° and were then diluted with a large volume of water. The liberated iodine was titrated with standard sodium thiosulfate solution. Using this procedure much higher values for the active oxygen content of the products were obtained than when less drastic methods[18] were employed.

The lead tetraacetate test for hydroperoxides[19] was negative when applied to the products of ozonization of hexamethylbenzene, mesitylene and benzene in acetic acid. The tests were conducted using acetic acid as the solvent for the lead salt.

The results of the experiments to establish the nature of the reaction products are summarized in Table III.

TABLE III

THE OZONIZATION PRODUCTS

Products	Method of identification	Yield,[a] %
Hexamethylbenzene in carbon tetrachloride		
Biacetyl	Isolated as the dioxime	6
Biacetyl	Visible spectrum[b]	9
Acetic acid	Alkalimetry[c]	4
Peroxidic material	Iodometric analysis[d]	55
Hexamethylbenzene in acetic acid		
Biacetyl	Visible spectrum[b]	18
Peroxidic material	Iodometric analysis[d]	75
Hexaethylbenzene in carbon tetrachloride		
Bipropionyl	Isolated as the dioxime	7
Bipropionyl	Isolated as the osazone	36
Propionic acid	Alkalimetry[c]	12
Mesitylene in carbon tetrachloride		
Methylglyoxal	Isolated as the dioxime	6
Acetic acid	Alkalimetry[c]	25
Peroxidic material	Iodometric analysis[d]	40
Mesitylene in acetic acid		
Peroxidic material	Iodometric analysis[d]	61
Benzene in carbon tetrachloride		
Peroxidic material	Iodometric analysis[d]	27

[a] The percentage yields apply to experiments in which considerably less than the stoichiometric quantity of ozone was absorbed by the aromatic hydrocarbon solution. It is assumed that in theory one mole of ozone should produce one mole of peroxidic product or one mole of dicarbonyl compound or two moles of aliphatic acid. Where solid derivatives were isolated, yields are based on the weight of the purified material. [b] Direct determination without reduction of peroxidic products. [c] The peroxidic products were reduced in aqueous medium. The resultant solution was acidified and distilled to remove organic acid. The distillate was titrated with standard base. [d] See ref. 17.

Results

The Reaction Kinetics.—In analyzing the kinetic data for the ozonization of the polyalkylbenzenes in carbon tetrachloride and in acetic acid, it has been assumed that one molecule each of the two reactants takes part in the slow step of the reaction (equation 6). Additional molecules ($n - 1$) of ozone are presumed to disappear in fast

$$-\frac{1}{n}\frac{d(O_3)}{dt} = -\frac{d(ArH)}{dt} = k(ArH)(O_3) \qquad (6)$$

follow reactions leading to the formation of product.[20] The corresponding integral rate law is

$$\log\frac{(ArH)}{(O_3)} = \frac{[n(ArH)_i - (O_3)_i]}{2.3}kt + \log\frac{(ArH)_i}{(O_3)_i} \qquad (7)$$

Evidence is presented in the Experimental section that n is close to 3, as has been reported by earlier investigators,[5,6,20] under the reaction conditions of the rate runs. Additional information concerning this value may be obtained from the analysis of rate runs in which both the ozone and alkylbenzene concentrations change markedly during the reaction. Figure 1 describes a run in acetic acid in which the initial ozone to mesitylene ratio is 2.0. A plot of log $(ArH)/(O_3)$ *versus* time, constructed on the assumption that $n = 3$, is linear as is required by equation 7. On the other hand a plot of $1/(O_3)$ *versus* time, constructed on the assumption that $n = 2$, is not linear (as would

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[15] P. W. Haajiman and J. P. Wibaut, *Rec. trav. chim.*, **60**, 851 (1941).

[16] J. G. Kirchner, A. N. Prater and A. J. Haagen-Smit, *Ind. Eng. Chem., Anal. Ed.*, **18**, 31 (1946).

[17] J. L. Warnell and R. L. Shriner, THIS JOURNAL, **79**, 3166 (1957).

[18] *Cf.* G. Blust and G. Lohaus, *Ann.*, **583**, 2 (1953).

[19] R. Criegee, *Fortsch. chem. Forsch.*, **1**, 508 (1950).

[20] This treatment follows that used previously in interpreting the results of other kinetic studies of aromatic hydrocarbon ozonization; J. P. Wibaut, F. L. J. Sixma, L. W. F. Kampschmidt and H. Boer, *Rec. trav. chim.*, **69**, 1355 (1951).

be required if (ArH) were equal to $(O_3)/^2$ throughout the run). Although, as described in the Experimental section, somewhat lower values of n were established through recovery of unreacted hydrocarbon from solutions which had been subjected to partial ozonization, a figure of $n = 3$ has been used in the interpretation of all of the kinetic data.

The rate constants, k, for reactions of the various alkylbenzenes in carbon tetrachloride and in acetic acid are given in Tables IV and V. In all cases they were evaluated graphically from the rate data (see Fig. 1—line I).

TABLE IV

RATE CONSTANTS FOR THE REACTION OF OZONE AND ALKYLBENZENES IN CARBON TETRACHLORIDE

Aromatic hydrocarbons	$10^3(ArH)_i$, mole l.$^{-1}$	$10^3(O_3)_i$, mole l.$^{-1}$	No. of runs	k, l. mole^{-1} sec.$^{-1}$
		25.2 ± 0.2°		
Benzene	10.6–42.6	0.245–1.53	6	0.028 ± 0.002
Toluene	4.26–17.0	.64–2.58	5	.166 ± 0.008
p-Xylene	0.577–2.33	.296–2.62	6	.95 ± 0.07
o-Xylene	1.19–2.38	2.47	2	.82 ± 0.05
m-Xylene	1.32–5.28	0.436–2.94	5	.78 ± 0.05
Mesitylene	0.535–1.21	.072–1.30	5	4.2 ± 0.4
Pseudocume	.443–0.886	.077–0.414	4	2.8 ± 0.3
Hemimellitene	.994	.614–2.49	3	2.8 ± 0.3
Durene	.134–0.538	.106–0.454	5	10.7 ± 0.2
Pentamethylbenzene	.034–0.137	.022–0.148	5	50 ± 3
Hexamethylbenzene	.015–0.033	.022–0.044	3	245 ± 13
Ethylbenzene	2.28–5.49	.195–2.85	6	0.34 ± 0.06
m-Diethylbenzene	1.05–2.10	.159–1.10	4	1.07 ± 0.11
sym-Triethylbenzene	0.324–1.30	.288–1.32	5	4.0 ± 0.4
1,2,4-Triethylbenzene	.427–0.854	.135–0.554	4	3.4 ± 0.1
1,2,3,4-Tetraethylbenzene	.262–0.525	.102–0.592	5	4.9 ± 0.5
1,2,4,5-Tetraethylbenzene	.281–0.563	.123–0.737	4	12.5 ± 1.5
Pentaethylbenzene	.086–0.346	.055–0.202	5	10.5 ± 0.4
Hexaethylbenzene	.859–1.72	.386–1.33	4	3.36 ± 0.11
Isopropylbenzene	2.32–9.27	.262–0.982	5	0.35 ± 0.02
m-Diisopropylbenzene	1.75–3.50	.178–0.975	4	1.0 ± 0.1
t-Butylbenzene	4.60–18.4	.275–2.58	5	0.069 ± 0.010
p-Di-*t*-butylbenzene	11.8–23.5	.176–1.11	4	0.157 ± 0.003
sym-Tri-*t*-butylbenzene	1.74–6.98	.242–1.01	5	0.33 ± 0.03
		11.2 ± 0.1°		
Toluene	8.52–17.1	0.365–0.391	2	0.0556 ± 0.0005
Ethylbenzene	5.67–11.3	.266–0.416	2	0.116 ± 0.001
Mesitylene	0.560	.085–0.111	2	1.75 ± 0.09
Hexaethylbenzene	.995	.547–0.651	2	1.32 ± 0.02
sym-Tri-*t*-butylbenzene	3.60–14.4	.144–0.770	5	0.125 ± 0.010
		2.2 ± 0.2°		
Benzene	85.8	1.90	1	0.00436

A considerable controversy has developed as to whether ozone makes a one-step attack on an unsaturated system at the bond with the lowest bond localization energy or whether in the rate-determining step electrophilic attack occurs at the position of lowest atom localization energy. The arguments have been reviewed recently by Bailey.[21,22] Regardless of which interpretation is preferred it should be recognized that in attacking benzene and its derivatives ozone must function as an electrophilic reagent since the rate of the reaction is enhanced by the presence of electron releasing substituents (*e.g.*, alkyl groups) on the aromatic nucleus. The results summarized in Tables IV and V, as well as those of previous studies[5-7] of alkylbenzene ozonization kinetics, emphasize this point. For example in carbon tetrachloride hexamethylbenzene is about 9000 times as reactive as benzene at 25°, and in acetic acid the reactivity ratio of these two compounds at 25° is about 22000/1. It is interesting, therefore, that the differences in rates of reaction of aromatic hydrocarbons in the two solvents are relatively small. The rate constants for benzene and hexamethylbenzene increase only 3.2 and 8.4 times, respectively, when the solvent is changed from carbon tetrachloride to acetic acid. Since reactions in which activation is accompanied by increased polarization of the reactants occur much more readily in the latter solvent than in the former, it seems doubtful that the activated complex for the slow step in aromatic ozonization can be highly ionic in nature.[23] It is also noteworthy that the reaction rates are relatively insensitive to the water content of the media. Within the limits of error the rate constant for benzene in carbon tetrachloride was unaffected by using water saturated rather than untreated solvent. The rate constant for reaction of benzene

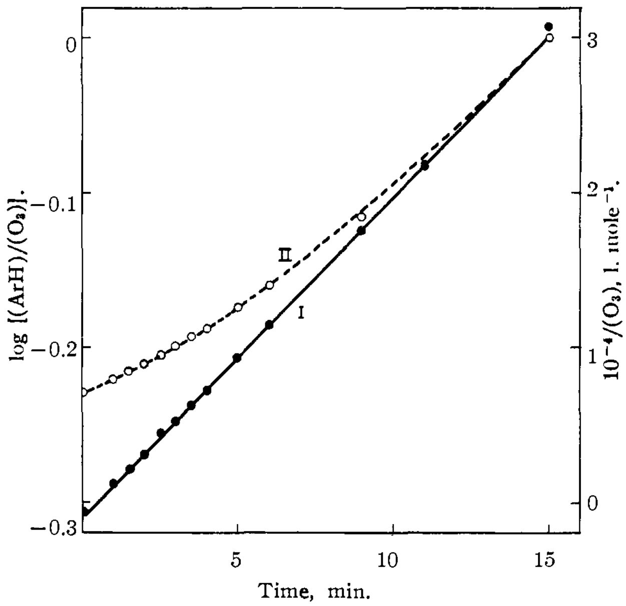

Fig. 1.—The reaction of ozone and mesitylene in acetic acid at 25.3°: $(O_3)_i = 1.40 \times 10^{-4}$ *M;* $(ArH)_i = 7.0 \times 10^{-5}$ *M.* Line I is referred to the left hand ordinate, with $n = 3$. Line II is referred to the right hand ordinate with $n = 2$. In constructing line I it was assumed that $(ArH) = (ArH)_i - [(O_3)_i - (O_3)]/3$. The points at $t = 15$ min. correspond to 76% reaction with respect to ozone.

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[21] P. S. Bailey, *Chemistry and Industry*, 1148 (1957).

[22] P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

[23] Note, however, that the ratio of rate constants for the reaction of benzene with ozone at −28° in nitromethane and in chloroform is about 30 (see ref. 7).

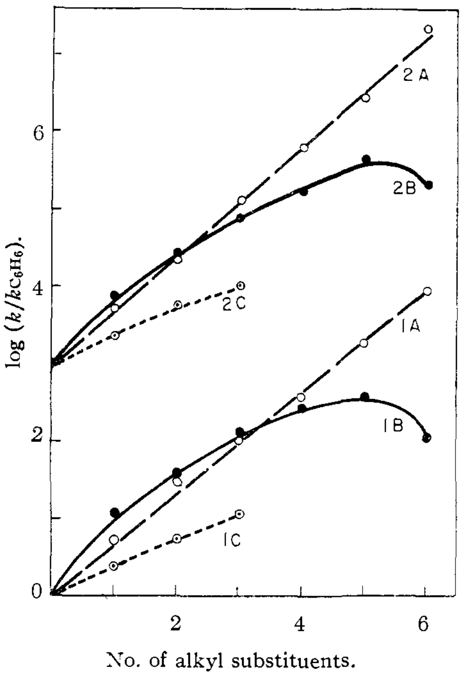


Fig. 2.—A plot of log ($k/k_{C_6H_6}$) (25°) *versus* the number of ring alkyl substituents. The lower series of curves are for the ozonations in carbon tetrachloride of methylbenzenes (1A), ethylbenzenes (1B) and *t*-butylbenzenes (1C). Average values of k from Table IV have been used when rate constants for more than one isomer were available. A similar treatment of the data of Table V for acetic acid solutions is presented in the upper set of curves (2 series). The ordinates have been displaced upward by 3 units from actual values for the 2 series of curves.

TABLE V

RATE CONSTANTS FOR THE REACTION OF OZONE AND ALKYLBENZENES IN ACETIC ACID

Aromatic hydrocarbons	$10^3(\text{ArH})_i$, mole l.$^{-1}$	$10^3(\text{O}_3)_i$, mole l.$^{-1}$	No. of runs	k, l. mole^{-1} sec.$^{-1}$
	25.2 ± 0.2°			
Benzene	9.10–36.3	0.504–3.63	5	0.091 ± 0.003
Toluene	1.55–6.22	.144–1.36	5	.50 ± 0.03
o-Xylene	0.537–2.15	.173–1.47	5	1.98 ± 0.13
Mesitylene	.070–0.279	.055–0.227	5	11.9 ± 0.5
Durene	.058–0.116	.046–0.117	3	59 ± 1
Pentamethylbenzene	.016–0.033	.024–0.044	3	250 ± 10
Hexamethylbenzene	.0156	.026	2	2050 ± 50
Ethylbenzene	.70–2.78	.232–1.15	5	0.67 ± 0.06
m-Diethylbenzene	.258–1.03	.148–0.551	5	2.26 ± 0.14
sym-Triethylbenzene	.175–0.701	.077–0.193	5	7.3 ± 0.2
1,2,3,4-Tetraethylbenzene	.113–0.236	.075–0.251	4	16.5 ± 1.1
Pentaethylbenzene	.084–0.175	.062–0.113	3	40.2 ± 0.4
Hexaethylbenzene	.135–0.539	.149–0.578	5	18.7 ± 2.4
Isopropylbenzene	.75–3.01	.223–1.14	5	0.72 ± 0.05
m-Diisopropylbenzene	.408–1.63	.255–1.22	5	2.1 ± 0.3
t-Butylbenzene	3.65–14.5	.296–1.91	5	0.205 ± 0.021
p-Di-*t*-butylbenzene	1.24–4.94	.246–1.67	5	0.51 ± 0.05
sym-Tri-*t*-butylbenzene	0.865–3.46	.170–1.68	5	0.90 ± 0.11
	17.7 ± 0.2°			
Ethylbenzene	1.32–2.64	0.29	2	0.37 ± 0.01
	18.0 ± 0.2°			
Toluene	2.99	0.198	2	0.291 ± 0.001
Mesitylene	0.141	.056–0.064	2	7.61 ± 0.01
sym-Tri-*t*-butylbenzene	3.51	.50	2	0.554 ± 0.005
	34.7 ± 0.2°			
Ethylbenzene	0.646	0.24	2	1.10 ± 0.04
	35.0 ± 0.2°			
Toluene	0.731–1.46	0.193	2	0.83 ± 0.02
Mesitylene	.069	.071	2	16.6 ± 0.1
sym-Tri-*t*-butylbenzene	.851	.67	2	1.71 ± 0.02
	44.0 ± 0.2°			
Toluene	0.722	0.198	2	1.41 ± 0.02
Mesitylene	.034	.061	2	26.7 ± 0.9
Ethylbenzene	.319	.22	2	2.02 ± 0.07
sym-Tri-*t*-butylbenzene	.836	.61	2	2.82 ± 0.05

in acetic acid containing 5 volume % of water was only 1.4 times as large as that obtained using dry acetic acid.

In Fig. 2 the logarithms of the ozonization rate constants relative to that of benzene at 25° for the polyalkylbenzenes which have been investigated are plotted against the number of alkyl substituents on the aromatic nucleus. Where data for more than one isomer were available, as in the case of the xylenes, the averages of the several log ($k/k_{C_6H_6}$), values has been plotted. Both for carbon tetrachloride and acetic acid media there is a reasonably good linear correlation between the logarithms of the relative reactivities of the polymethylbenzenes and the number of ring methyl substituents. In other words, discounting relatively minor positional effects of substituents, the contributions of all individual methyl groups to the total free energy of activation are additive. The same statement may be applied in summarizing ethyl substituent effects, excluding pentaethyl- and hexaethylbenzene reactivities. It should be noted in comparing lines 2A and 2B and 1A and 1B of Fig. 2 that the points on which the A and B series curves are based do not always encompass the same set of positional isomers. In most instances the polyethylbenzenes (through the tetrasubstituted benzenes) are slightly more reactive than their correspondingly substituted polymethylbenzenes. Thus in carbon tetrachloride relative reactivities are in the order ethylbenzene > toluene, *m*-diethylbenzene > *m*-xylene, mesitylene∼*sym*-triethylbenzene. The relative reactivities of isopropyl- and *m*-diisopropylbenzenes are almost identical with those of the corresponding ethylbenzenes. Clearly the reactivity of hexaethylbenzene is abnormally low (of the order of 1/100 that of hexamethylbenzene in both solvents). Since the less highly alkylated methyl- and ethylbenzenes are of comparable reactivity, the unfavorable rate effect of packing the aromatic nucleus with ethyl substituents must be purely steric in origin. Pentaethylbenzene, which is of the order of 1/5 as reactive as pentamethylbenzene, may also be subject to some steric deactivation. The suppressed reactivities of the *t*-butylbenzenes (curves 1C and 2C, Fig. 2) as compared to those of the corresponding methylbenzenes must also be steric rather than electronic in origin. The alternate explanation that *t*-butyl substituents, unlike methyl substituents, cannot contribute to hyperconjugative stabilization in the transition state of an electrophilic substitution reaction,[24] does not seem applicable. Were this the case one would expect that mono- and dimethylbenzenes would be more reactive than the corresponding ethyl and isopropyl derivatives, which they are not.

Qualitatively the effects (both electronic and steric) of ring substituents on ozonization rates, as depicted in Fig. 2, are strikingly similar to the effects of these same substituents on the stabilities of iodine and iodine monochloride complexes in carbon tetrachloride.[1-3] Actually on a plot of the logarithms of equilibrium constants for formation of the polyalkylbenzene–iodine monochloride complexes *versus* the number of donor ring substituents,[3] the only points which fall very short of the straight line which best accommodates the data are those for hexaethylbenzene and *sym*-tri-*t*-butylbenzene.

Energies and Entropies of Activation.—Where rate constants at two or more temperatures have been obtained (Tables IV and V) energies and entropies of activation for the ozonization reactions have been calculated (see Table VI). Although the variations in energies of activation are not large for the series of compounds for which figures are available, they seem, in the absence of steric problems, to diminish as the number of alkyl groups on the aromatic nucleus is increased. The E_a value for mesitylene is over 2 kcal. less than that for toluene both in carbon tetrachloride and in acetic acid. Unfavorable steric effects of alkyl substituents on reaction rates are also reflected in E_a. The value of hexaethylbenzene in carbon tetrachloride is actually somewhat larger than that for mesitylene. Little significance can be placed on the variations in entropies of activation for the several reactions summarized in Table VI, since the variations are of the order of magnitude of the errors in reported values.

TABLE VI

ENERGIES AND ENTROPIES OF ACTIVATION FOR OZONIZATION

	CCl_4[a]		HOAc[a]	
Hydrocarbon	E_a, kcal.	$-\Delta S^*$, e.u.	E_a, kcal.	$-\Delta S^*$, e.u.
Benzene	13.2	23	..	..
Toluene	13.2	20	11.1	25
Mesitylene	10.7	22	8.8	26
Ethylbenzene	13.1	19	11.6	26
Hexaethylbenzene	11.4	20	..	..
sym-Tri-*t*-butylbenzene	11.7	23	11.8	21

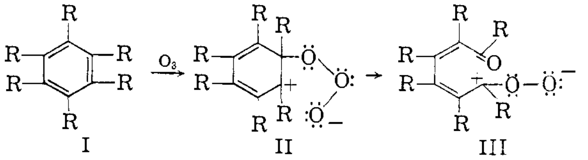
[a] Values listed for carbon tetrachloride solution were calculated from rate constants at two different temperatures, which except in the case of benzene, differed by only 14°. The reported values for acetic acid are based in most cases on Arrhenius plots covering three or four different temperatures.

The Reaction Products.—The products of ozonization of benzene and its polymethyl derivatives in solution at temperatures below 0° have been examined extensively by previous investigators,[25] but no information concerning the nature of products as formed in the temperature range of this investigation has been reported. Accordingly the compositions of product mixtures formed by ozonization of a few polyalkylbenzenes in carbon tetrachloride and acetic acid at room temperature have been checked. These mixtures were complex in nature, and those components which were separated were obtained only in poor yields. The experimental findings have been summarized in Table III of the Experimental section, where pertinent details of product separation and identification already have been discussed.

On ozonization of hexamethylbenzene, hexaethylbenzene or mesitylene in carbon tetrachloride and of hexamethylbenzene, mesitylene or benzene in acetic acid substantial quantities of active oxygen containing compounds were formed as was established by iodometric methods. The acetic acid solutions of the reaction products tested negatively for hydroperoxides.[19] The test is, however, not completely reliable.[26]

From the hydrolysates of the products of ozonolysis of hexamethylbenzene in carbon tetrachloride, biacetyl, identified as its dioxime, and acetic acid, identified as the *p*-phenylphenacyl derivative, were obtained. The diketone was also isolated under hydrolytic conditions when acetic acid was used as the medium for ozonization. Similarly bipropionyl and methylglyoxal were identified in the hydrolysates of the products of ozonolysis of hexaethylbenzene and mesitylene, respectively, in carbon tetrachloride. Propionic acid was also found in analyzing the hexaethylbenzene reaction products. The temperature at which the ozonization is conducted apparently does not have a pronounced effect on the nature of the reaction products, since diketones and aliphatic acids are also the major isolable materials resulting from alkylbenzene ozonization below 0°.[25]

The results of the kinetic and product studies can be rationalized reasonably well in terms of the general views of Criegee concerning the mechanism of ozonolysis as applied to aromatic systems.[25] The bimolecular reaction of ozone with polyalkylbenzene (I), which has been presumed to be rate determining in the analysis of the kinetic data, may lead to an intermediate II which is capable of rapid rearrangement to the Criegee zwitterion III. The structure of II may be formulated alternately,[21,22] and the authors have no firm convictions on this point. Zwitterion III, a diene which is certainly extremely susceptible to further reaction with two additional molecules of ozone,[27] may furnish IV, V and VI.



I II III

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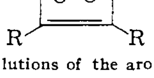
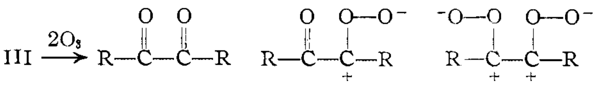
[24] H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

[25] Their findings have been summarized by Bailey; see ref. 22, p. 958.

[26] Ref. 22, p. 987.

[27] It is possible that III might rearrange to  In this way one double bond might be lost by a process not involving ozone. This type of rearrangement apparently does not occur under the conditions of the rate runs. It should be noted, however, that such a process might be considered in explaining the fact that values of $n < 3$ were obtained in experiments in which concentrated solutions of the aromatic hydrocarbons were underozonized (see the Experimental section).

Because of its unfavorable charge distribution VI seems unlikely as a reaction intermediate. Yet IV cannot be formed unless VI also is formed, and evidence is presented in the Experimental section that biacetyl can be produced directly by ozonization of hexamethylbenzene (either in carbon tetrachloride or acetic acid) without hydrolysis of the reaction products. Products V and VI may be presumed to undergo polymerization to form polymeric peroxides or, in acetic acid, to form hydroperoxides by reaction with the solvent. On hydrolysis under reducing conditions these compounds should break down to diketone IV. In one variation of the suggestions concerning the reaction mechanism intermediate III may be pictured as undergoing polymerization or reaction with hydroxylic solvent before its double bonds are attacked by ozone.



$$\mathrm{III} \xrightarrow{2O_3} \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}R} \qquad \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\underset{+}{\overset{\overset{O-O^-}{|}}{C}}{-}R} \qquad \mathrm{R{-}\underset{+}{\overset{\overset{^-O-O}{|}}{C}}{-}\underset{+}{\overset{\overset{O-O^-}{|}}{C}}{-}R}$$

IV V VI

Product V is very likely susceptible to rearrangement to the isomeric anhydride,[28] IV. It is therefore reasonable that, as is the case, acetic acid should be obtained by hydrolysis of the ozonization products of hexamethylbenzene and mesitylene in carbon tetrachloride and that propionic acid should be obtained similarly from hexaethylbenzene. It is noteworthy, however, that acetic acid has been detected, by gas–liquid chromatography, as an immediate product of reaction of mesitylene and ozone in carbon tetrachloride. It is conceivable that this acid was formed by thermal decomposition of a reaction product at the relatively high temperature (~100°) of the chromatograph column.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

[28] R. Criegee and M. Lederer, *Ann.*, **583**, 29 (1953).

Davis, California

[Contribution from the Department of Physical Chemistry, Hebrew University]

The Kinetics of the Oxidation of D-Glucose by Bromine and by Hypobromous Acid

By B. Perlmutter-Hayman and A. Persky

Received July 6, 1959

The kinetics of the oxidation of D-glucose by aqueous bromine solutions has been reinvestigated. From the dependence of the rate of reaction on bromide concentration it was concluded that molecular bromine is the oxidizing agent, tribromide and hypobromous acid making only negligible contributions. This was confirmed by the slowness of the reaction of hypobromous acid with glucose. The dependence of the reaction rate on *p*H is consistent with the assumption that the anionic form of glucose is oxidized much faster than glucose itself.

The oxidation of D-glucose by bromine has been the subject of several investigations.[1-4] Bunzel and Mathews[2] studied the kinetics in dilute acid solutions and interpreted their results on the assumption that OH^- takes part in the rate-determining step. Isbell and Pigman[3] carried out an extensive study at the *p*H of a $BaCO_3$–CO_2 mixture. The dependence of the rate on bromide concentration pointed to free bromine as the only oxidizing agent. The primary product was the δ-lactone of gluconic acid. Furthermore, β-D-glucose was found to react about 35 times faster than the α-form. More recently[4] it was concluded from the strong increase of the rate with increasing *p*H that hypobromous acid is the oxidizing agent in bromine water.

In view of these discrepancies and as a continuation of our program[5-7] to investigate the specific oxidizing properties of bromine and of hypobromous acid it seemed interesting to reinvestigate the oxidation of D-glucose by bromine water, measuring *both* the dependence on bromide concentration and on *p*H. A direct measurement of the rate of reaction between hypobromous acid and glucose also seemed desirable.

Experimental

The experiments were carried out at 0°, in glass-stoppered erlenmeyer flasks immersed in a Dewar bottle containing ice and water. The progress of the reaction was followed by iodometric titration, using 0.01 *N* thiosulfate solution. The *p*H was measured at the beginning and at the end of each reaction, using a Beckman Model G *p*H-meter. Unless otherwise stated, it changed by less than 0.1 unit. The buffers used were Na_2HPO_4–NaH_2PO_4, sodium acetate–acetic acid, NaH_2PO_4–phosphoric acid, and appropriate concentrations of sulfuric acid, thus covering the desired *p*H range.

Hypobromous acid solutions were prepared as usual.[6] All the reagents were "Analar"-grade. The α-D-glucose was Hopkin and Williams, and the β-D-glucose Nutritional Biochemical Corporation.

The concentration of the oxidizing agent was between (5 to 10) × 10^{-3} *M*, and that of D-glucose was always in excess and was varied between 0.025 and 0.500 *M* according to conditions, in order to get convenient reaction rates.

When experiments were repeated, their rate constants agreed within less than ±3%.

Rate constants are expressed in mole^{-1} l. min.^{-1}.

Results

1. The Oxidation of α- and of β-D-Glucose, and the Influence of Anomerization.

—At *p*H 4.95,

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[1] J. W. Green, *Advances in Carbohydrate Chem.*, **3**, 129 (1948).

[2] H. H. Bunzel and A. P. Mathews, This Journal, **31**, 464 (1909).

[3] H. S. Isbell and W. Pigman, *J. Research Natl. Bur. Standards*, **10**, 337 (1933); **18**, 141 (1937).

[4] K. C. Grover and R. C. Mehrotra, *Z. physik. Chem. (Frankfurt)*, **14**, 345 (1958).

[5] L. Farkas, B. Perlmutter and O. Schächter, This Journal, **71**, 2829 (1949).

[6] Y. Knoller and B. Perlmutter-Hayman, *ibid.*, **77**, 3212 (1955).

[7] L. Binoun and B. Perlmutter-Hayman, *Bull. Research Council Israel*, **A5**, 52 (1955).