

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CORNELL AND PRINCETON UNIVERSITIES]

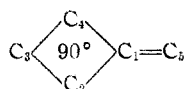
The Structures of Methylene-cyclobutane and Hexamethylethane

BY S. H. BAUER AND J. Y. BEACH

In this paper we are reporting an electron diffraction investigation of two hydrocarbons, methylenecyclobutane and hexamethylethane. Although the configuration of both compounds is known from chemical data and no unusual bond distances were expected, this study was nevertheless undertaken to verify the presence of 90° C-bond angles in the first of these and to establish the relative orientation of the methyl groups in the second. Both compounds were furnished by Dean F. C. Whitmore, to whom we wish to express our sincerest thanks.

Methylenecyclobutane

The physical constants of the material used were: b. p. 41.3° (746 mm.); n_D^{20} 1.4204. Its configuration had been determined by ozonization. The electron diffraction photographs were obtained in the usual manner and analyzed according to the visual method.¹ The appearance of the pattern is close to that indicated by curve B of Fig. 1, superposed on a continuously decreasing background. The $s_0 [= (4\pi/\lambda) \sin \theta/2]$ values and the relative intensities of the maxima and minima are given in Table I. The radial distribution curve (R. D. of Fig. 1) can be interpreted readily in terms of the planar model



using the generally accepted C—C, C=C, and C—H distances (heavy vertical lines under curve R. D.). However, due to the poor resolution of the density peaks, accurate deductions regarding various structural features, such as values for the ratio C—C/C=C or for the angles in the ring, cannot thus be obtained.

Intensity curves were computed for various bonding angles, C—C/C=C ratios, etc., with C—H assumed to be 1.09 Å., $Z_H = 1.25$. Of these, the two calculated patterns which were in best agreement with the one observed were for the models:

$$\begin{aligned} \text{C—C/C=C} &= 1.54/1.30 \text{ (B, Fig. 1)} \\ &= 1.54/1.34 \text{ (C)} \end{aligned}$$

in both $\angle\text{HCH} = 120^\circ$;² $\angle\text{HCC} = 109\frac{1}{2}^\circ$; angles in ring = 90° , and all carbon atoms coplanar. The quantitative comparison is presented in Table I. From it one may conclude that the best values for the interatomic distances in this compound as deduced from our data, are

$$\begin{aligned} \text{C—C} &= 1.56 \pm 0.03 \text{ \AA.} \\ \text{C=C} &= 1.34 \pm 0.02 \end{aligned} \quad \angle\text{C}_1\text{C}_2\text{C}_3 = 90^\circ; \text{ etc.}$$

TABLE I
METHYLENOCYCLOBUTANE

Max.	Min.	s_0	I_0	$s_0/s_0(\text{B})$	$s_0/s_0(\text{C})$	$s_0(\text{B}_5\text{H}_9)^3$
1		5.70	25	(1.053)	(1.044)	3.36
	2	7.66	-15	(1.056)	(1.050)	
2		9.26	15	1.015	1.011	5.34
	3	10.92	-10	0.993	1.004	6.80
3		12.22	10	1.042	1.038	8.00
	4	13.50	-3	1.059	1.032	9.67
4		14.62	3	1.031	1.016	11.49
	5	15.87	-5	1.021	1.013	
5		17.13	5	1.039	1.048	15.61
	6	21.99	1	0.964	0.965	
Average				1.020	1.016	
Av. dev.				0.022	0.018	
Interatomic						
distances		C—C		1.57	1.56	
deduced, Å.		C=C		1.33	1.36	

Discussion.—Methylenecyclobutane appears to be the first compound with a four-membered carbon ring for which interatomic distances and bond angles have been determined. Although the rather unusual 90° valence angles for carbon are to be expected in the cyclobutanes, it was of interest to demonstrate in at least one instance that such was the case.

The electron diffraction patterns of C_6H_8 and B_5H_9 are very much alike; the predicted differences in shape of the first and fourth maxima due to (1) differences in the ratios (Z_C/Z_H) and (Z_B/Z_H), and (2) the relatively shorter handle of the carbon ring as compared with the boron ring, have been checked. This lends further confirmation to the methylenecyclobutane-like structure assigned to the pentaborane by Bauer and Pauling.³

(2) We assumed that the $\angle\text{HCH}$'s were stretched to 120° to compensate for the compression of the $\angle\text{CCC}$'s in the ring; the pattern would not be altered appreciably if the value 110° were selected instead.

(3) S. H. Bauer and L. Pauling, *THIS JOURNAL*, **58**, 2403 (1936).

(1) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

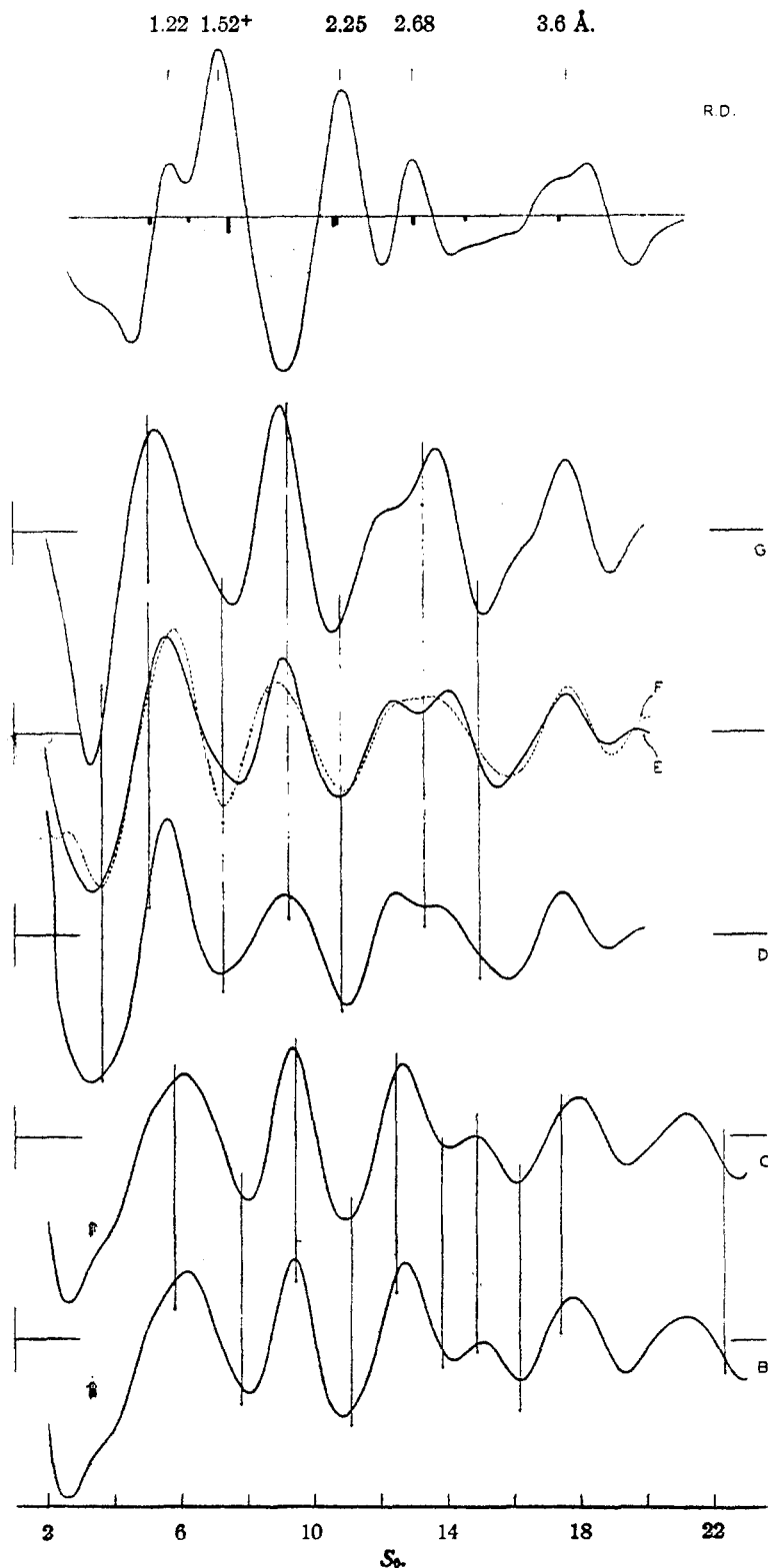


Fig. 1.—Methylenecyclobutane and isomers: Curve RD, radial distribution curve; Curve B, methylenecyclobutane, square four-membered ring, tetrahedral angles otherwise, C—C/C=C = 1.54/1.30, C—H = 1.09; Curve C, same as B, but C—C/C=C = 1.54/1.34; Curve D, vinylcyclopropane (C—C = 1.54, C—H = 1.09), orientation for maximum distance between hydrogen atoms; Curve E, 1-methylcyclobutene (1); Curve F, 2-methylcyclobutene (1); Curve G, spiro-pentane. Top set of vertical lines indicate Rogowski's s_0 values; bottom set, our data.

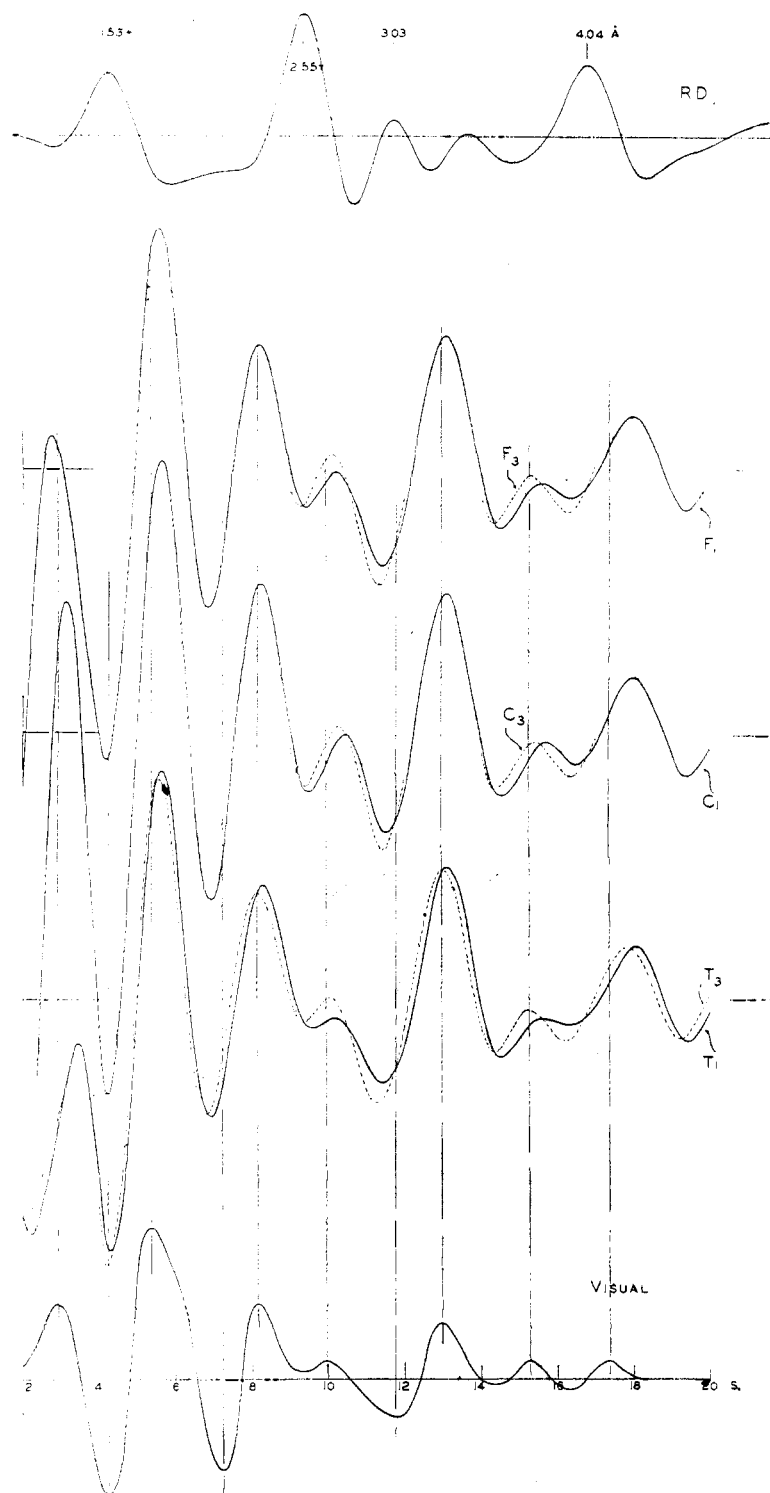
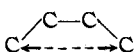
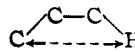


Fig. 2.—Hexamethylethane: Curve R. D., radial distribution; Curve T₁, staggered configuration of  and  with all C—C = 1.54, C—H = 1.09 and all angles tetrahedral; temperature and damping factors as given in text; Curve T₃, staggered configuration, C_α—C_β = 1.60 and ∠CC_αC = 111°; Curve C_{1,3}, as above, respectively, but eclipsed configurations; Curve F_{1,3}, as above, respectively, but freely rotating groups.

As was stated above, the configuration of this compound was deduced by Prof. F. C. Whitmore and P. H. Williams by ozonolysis. Further confirmation that the material used was not one of the several isomers of methylenecyclobutane which have boiling points close to 42° came from a comparison of the intensity of diffraction curves computed for vinylcyclopropane, 1-methylcyclobutene (1), 2-methylcyclobutene (1), and spiro-pentane (curves D, E, F and G of Fig. 1, respectively), with the pattern observed. The crucial regions of comparison are the first and third peaks; whereas curves B and C, in agreement with observation, indicate a shoulder on the left of the first peak, and show the third peak *steep on the left*, but accompanied by a *weak fourth maximum on the right*, the other curves suggest no such features. Furthermore, it appears that no reasonable variation of the parameters for the latter models (D to G) could bring them into agreement with the data.

The case of spiro-pentane is of special interest. Although a number of chemists have expressed doubt as to whether the synthesis of the compound has been accomplished, F. Rogowski⁴ claims that he prepared this substance by treating pentaerythrityl tetrabromide with an excess of zinc dust in 50% alcohol (b. p. of final product 39.5°), and verified its structure by an electron diffraction study. Unfortunately, considerable doubt is cast on his work⁵; he does not clearly state that he had analyzed his product to prove that it was pure and of the composition C_5H_8 ; he does not give its index of refraction nor does he describe the qualitative features of the diffraction photographs. Were one to assume that Rogowski's preparation was satisfactory, and that his s_0 values (computed from the ring diameters, nozzle-plate distance, and accelerating potential quoted by R.⁴) are characteristic of a pure substance of composition C_5H_8 with a boiling point in the neighborhood of 40° , one would conclude from a comparison of these s_0 values with the curves B to G (Fig. 1) that he did not have methylenecyclobutane nor 1-methylcyclobutene(1); that if the best quantitative agreement is used as the *sole*

(4) F. Rogowski, *Ber.*, **72**, 2021 (1939).

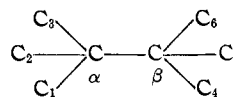
(5) Private communication from Frank C. Whitmore and P. H. Williams: "2300 g. of pentaerythrityl tetrabromide (m. p. $159-160^\circ$) were treated with an excess of zinc dust in 50% aqueous methanol; 204.5 g. of methylenecyclobutane, b. p. 41.3° (746 mm.) and n_D^{20} 1.4203-6 together with 18.5 g. of 2-methyl-1-butene, boiling at $30-31^\circ$ (737 mm.) and n_D^{20} 1.3780-1.3805 resulted. Both compounds were identified by ozonolysis. In spite of intensive searches, no evidence of the presence of any other compound was found."

criterion, he did have spiro-pentane; but that in the absence of a full description of the observed pattern, particularly the structure of the third maximum, one cannot state that either 2-methylcyclobutene(1) or vinylcyclopropane has been unquestionably eliminated. A plausible explanation for the difference between our data and those of Rogowski is that he had a mixture of methylenecyclobutane and 2-methyl-1-butene. The diffraction curve for the latter would be quite similar to D (Fig. 1), and it is apparent that a considerable admixture of D with B would result in a curve which would fit his s_0 values.

In our computations we did not consider cyclopentene (b. p. $44.1-44.6^\circ$), 1-methyl nor 2-methylenecyclopropane, nor chain isomers of C_5H_8 .

Hexamethylethane

The electron diffraction photographs obtained for hexamethylethane (sample at 85° during run) appear to the eye as indicated by curve V of Fig. 2, superposed on a continuously decreasing background. The observed s_0 values and estimated relative intensities of the maxima and minima are summarized in Table II. The radial distribution curve calculated according to the method of Walter and Beach⁶ is shown in Fig. 2, curve R. D. The peak at $2.55 + \text{\AA}$. as well as the one at $1.53 + \text{\AA}$. is symmetric and sharp. One should note that for a C—C separation of 1.54\AA . and tetrahedral valence angles a peak is to be expected at 2.51\AA . This difference between the computed and observed positions suggests a lengthening of the C—C bond, or an increase in the $C_2C_\alpha C_3$ valence angle, or both. The last possibility might be ex-



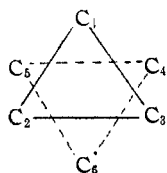
pected if the conclusions of Brown *et al.*⁷ regarding the influence of substituting methyl groups on the strength of the B—N bond may be extended to the C—C bond. Effects on the length of the $C_\alpha-C_\beta$ bond due to differences in hyperconjugation between H_3C-CC_3 and C_3C-CC_3 are too small to be detected, since Pauling and Brockway⁸ report finding the C—C separation in neopentane equal to that in ethane.

(6) J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940).

(7) H. C. Brown, H. I. Schlesinger and S. Z. Cardon, *THIS JOURNAL*, **64**, 325 (1942).

(8) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

If the radial distribution curve were completely integrated so that extra minima, particularly those which are always present on each side of a maximum, did not appear, the probability distribution in angle of $C_{1,2,3}$ about the symmetry axis could be read directly from the R. D. curve.⁹ Under the present circumstances one may readily interpret the peak at 3.03 Å. as the scattering due to interactions of the type C_1-C_4 , C_1-C_5 , etc., and



the peak at 4.04 Å. resulting from the contribution of C_1-C_6 , etc. (expected 3.87 Å.), but no estimate of the relative importance of the eclipsed and staggered configurations can be made.

Since the number of parameters determining the structure of hexamethylethane is large, we attempted to get the best fit between the observed and predicted intensity curves by making the more elaborate calculations which include ($Z - f$), temperature factors and the approximate expressions developed by Debye⁹ for the cases of free rotation and torsional oscillations. In all, nine curves were computed, three each for the staggered (T) and eclipsed (C) configurations, and for free rotation about the various C-C bonds. For each of these possibilities:

Curve	Distances considered	Temp. factor	Remarks
1	all C-C = 1.54 all H-C = 1.09 all angles tetrahedral	0.0015 .0022	
	2.16	.0043	
	1.79	.0050	
	2.51	.0022	
	.0043	.0025	Distances and extra damping factors depending on whether T, C or F models used ⁹
	.0025		

For T and C, $\frac{V}{kT} = 9$, was assumed in computing the damping factors.⁹

All other terms were neglected due to their large temperature factors.

2 As above, except $C_\alpha-C_\beta$ was stretched to 1.58. This stretched half of the $C \leftrightarrow C$ terms to 2.55.



3 As in curve 1, but $C_\alpha-C_\beta$ was stretched to 1.60, and the valence angles on C_α, C_β extended to 111° . This stretched all of the $C \leftrightarrow C$ terms to 2.55.



It is clear from the curves in Fig. 2 that the differences between the various models are indeed small. However, careful comparisons of the qualitative features of the computed and observed curves, particularly in the region of the first, fourth and sixth maxima and the condition for least average deviation of the individual rings from the mean, suggest that the staggered configuration is probably most like that actually present in the molecule. This would be expected were one to extend the electron diffraction results previously obtained for 1,2-dichloro-¹⁰ and 1,1,2-trichloroethane,¹¹ to hexamethylethane. However, whichever one of the three configurations one selects, assuming that the central $C_\alpha-C_\beta$ bond is somewhat stretched (cases 2 and 3) improves the agreement with the observed curve. This can best be seen from the coincidence of the peaks with the vertical lines in Fig. 2, and from a comparison of the relative mean deviations of the more accurately measurable peaks in Table II, where the data for the staggered curve are pre-

TABLE II
HEXAMETHYLETHANE

Max.	Min.	s_0	I_0	$s_0(T_1)/s_0$	$s_0(T_2)/s_0$	$s_0(T_3)/s_0$	
1		2.935	10	(1.175)	(1.165)	(1.155)	
	2	4.246	-15	1.013	1.001	0.996	
2		5.377	20	1.049	1.041	1.030	
	3	7.233	-12	0.958	0.950	0.944	
3		8.151	10	1.014	1.006	0.999	
4		9.950	3	1.022	1.016	1.011	
	5	11.79	-5	0.969	0.964	0.959	
5		12.97	7	1.012	1.005	1.001	
6		15.28	2.5	1.021	1.010	0.998	
7		17.37	2.5	1.040	1.033	1.026	
				Average	1.011	1.003	0.996
Av. dev. (all but 1st max.)					.0210	.0208	.0198
Av. dev. (3rd-6th max., best measured region)					.0152	.0146	.0136
Interatomic distances							
deduced:				$C_\alpha-C_\alpha$, Å.	1.557	1.545	1.533
				$C_\alpha-C_\beta$, Å.	1.557	1.585	1.594
(assumed)				$\angle CC_\alpha C$	$109\frac{1}{2}$	$109\frac{1}{2}$	111°
(assumed)				C-H, Å.	1.09		

sented in detail. Similar improvement is found for the other models. The results deduced from the R. D. curve are thus supported. To summarize: in hexamethylethane, all C-C bond dis-

(10) J. Y. Beach and K. J. Palmer, *ibid.*, **6**, 639 (1938).

(11) A. Turkevich and J. Y. Beach, *THIS JOURNAL*, **61**, 3127 (1939)

(9) P. Debye, *J. Chem. Phys.*, **9**, 55 (1941).

tances but the central one ($C_{\alpha}-C_{\beta}$) are $1.54 \pm 0.02 \text{ \AA.}$; it is very likely that the central C-C bond distance is somewhat longer, $1.58 \pm 0.03 \text{ \AA.}$ and that the C_{α} , C_{β} valence angles are somewhat larger than tetrahedral, $111 \pm 2^{\circ}$.

Summary

The structures of methylenecyclobutane and hexamethylethane have been investigated by means of electron diffraction. The final results are: in methylenecyclobutane the carbon atoms are coplanar, four of them situated on the average at the corners of a square ($1.56 \pm 0.03 \text{ \AA.}$ on side), the fifth on an extension of one of the diagonals

($1.34 \pm 0.02 \text{ \AA.}$ from the carbon atom in the ring); for hexamethylethane the theoretical intensity curves for free rotation, and for the eclipsed and staggered configurations differ by very little, yet agreement with observation is slightly better for the staggered model. However, regardless of which one of these three models one uses, assuming that the central C-C bond is somewhat stretched ($1.58 \pm 0.03 \text{ \AA.}$) improves the correlation with the observed curve. The other distances are: C-C = $1.54 \pm 0.02 \text{ \AA.}$; carbon valence angles $111 \pm 2^{\circ}$; C-H = 1.09 \AA. (assumed).

ITHACA, N. Y.

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[FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

Kinetics and Mechanism of 2,6-Di-iodotyrosine Formation¹

BY CHOH HAO LI

Introduction

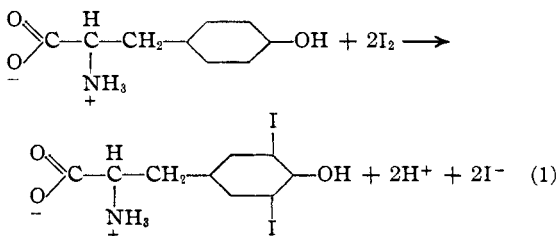
The halogenation of phenols has been examined by many investigators and yet no agreement has been reached with regard to the mechanism of the reactions. Baines^{1a} concluded that the active brominating agent was hypobromous acid but later Francis² showed that the aqueous bromination is due to the free bromine. Soper and Smith³ demonstrated from their chlorination studies that hypochlorous acid reacts with the phenoxide ion but it does not react with the un-ionized phenol or ether. On the other hand, chlorine can chlorinate the ether as well as the phenol.

The mechanism of the iodination of phenols is more confusing. The earlier investigations of Cofman⁴ gave the conclusion that the active iodinating agent was hypoiodous acid, free iodine having apparently no direct iodinating effect. He concluded further that the positive iodine ion is the halogenating agent. Later, Soper and Smith⁵ showed that the iodination of phenol is not caused by the positive iodine ion, but that the main reactions are those between the hypoiodous acid and the ionized and un-ionized phenol. Recently, Hunter and Budrow⁶ were able to iodinate pheno-

lates under anhydrous conditions. In this paper the kinetic data of the di-iodotyrosine formation suggest that the iodination of phenols may involve four paths, namely, (1) iodine and phenol, (2) iodine and phenolate, (3) hypoiodous acid and phenol, and (4) hypoiodous acid and phenolate. The importance of each path is determined by the pH and iodide ion concentrations. Thus, path (4) is the main path in the formation of iodinated phenol in slightly alkaline solution. On the other hand, path (2) leads to the results of Hunter's experiments.

Results

The Rate Law.—Tyrosine is a para substituted phenol; it has a dissociation constant between those of *p*-cresol and phenol.⁷ Its reaction with iodine may be represented by the equation



The product, 2,6-di-iodotyrosine, is shown to be a much stronger acid.⁸ Since the rate of halogenation changes with the pH of the solvent (see below), the reaction must be studied in a buffered

(1) Aided by grants from the Board of Research of the University of California and the Rockefeller Foundation, New York City, and Parke, Davis and Company, Detroit, Michigan

(1a) Baines, *J. Chem. Soc.*, 2810 (1922).

(2) Francis, *THIS JOURNAL*, 47, 2340 (1925).

(3) Soper and Smith, *J. Chem. Soc.*, 1582 (1926).

(4) Cofman, *ibid.*, 1040 (1919).

(5) Soper and Smith, *ibid.*, 2757 (1927).

(6) Hunter and Budrow, *THIS JOURNAL*, 55, 2122 (1933).

(7) Hitchcock, *J. Gen. Physiol.*, 6, 747 (1925).

(8) Kirk, Dawson and Schmidt, *J. Biol. Chem.*, 88, 589 (1930).