is slow compared to the rate of polymerization. Thus, although the thermodynamically stable state under the conditions indicated appears to be 0.004% $SiO_2$ as monomer, the rate of polymerization is so fast as compared with the rate of depolymerization that polymerization to higher intermediate polymers takes place before the stable state is reached.

**The Effect of Catalysts on Polymerization of Monosilicic Acid.**—Experiments studying the effect of catalysts confirm results reported by Iler[2] regarding fluoride. Thus, the most active catalyst found was the fluoride ion, which, when added to the extent of one or two parts per million, doubles the rate of polymerization of silicic acid at $p$H 2.9 and 1.90°. This effect of fluoride ion is counteracted by the addition of 10 parts per million of aluminum ions, presumably due to the formation of the complex fluoaluminate ion.

The action of a wide variety of inorganic and organic compounds was investigated, but none of the materials investigated had a very profound effect, in the $p$H range of 2-3. Specifically, molybdic acid at 0.001 $M$ or mannite at 10% increased the rate of polymerization slightly, but nickel sulfate, ferrous sulfate, silver nitrate, copper sulfate, at 0.00006 $M$, aluminum sulfate or phosphoric acid at 0.001 $M$, or sodium thiocyanate, potassium bromide, beryllium sulfate, boric acid, stannic chloride, titanium sulfate, at 0.02 $M$, had no effect. The addition of 10% methyl alcohol caused a slight decrease in the polymerization rate.

**Strength of Silicic Acids.**—It was found that monosilicic and polysilicic acids are very weak acids, since they apparently do not contribute any appreciable hydrogen ion concentration to their solutions. Thus, when a solution of 0.1 $M$ silicic acid was prepared in a solution of dilute $H_2SO_4$ of $p$H 2.10, the $p$H of the resulting silicic acid solution (after complete removal of $Na^+$ by ion exchange) was 2.10. Moreover, when a monomer solution was prepared at $p$H 2 and then adjusted to $p$H 3.89 by the addition of a trace of sodium metasilicate, it was found that, in spite of the fact that the degree of polymerization increased from 1.34 to over 5, the $p$H remained constant. These observations agree with the values of dissociation constants of orthosilicic acid reported to be $10^{-9.8}$ and $10^{-12.16}$[7]

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[7] P. S. Roller and Guy Ervin, Jr., THIS JOURNAL, **62**, 461 (1940).

WILMINGTON 98, DEL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

# An Electron Diffraction Investigation of the Molecular Structure of Hexafluoroethane[1]

BY JAMES L. BRANDT AND R. L. LIVINGSTON

RECEIVED SEPTEMBER 8, 1953

The interatomic distances in hexafluoroethane have been determined by electron diffraction using the visual correlation procedure. The following results were obtained: C–F = 1.330 ± 0.015 Å., C–C = 1.51 ± 0.06 Å., and ∠FCF = 108 ± 1.5°. The results are compared with two earlier electron diffraction investigations.

A previous electron diffraction investigation[2] of the structure of hexafluoroethane gave C–C = 1.45 ± 0.06 Å., C–F = 1.35 ± 0.02 Å., and ∠FCF = 107.5 ± 1.5°. Even with the rather large uncertainty on the C–C bond distance, these results indicated that this distance is considerably shorter than the value of 1.535 Å. found in ethane.[3] A second electron diffraction investigation[2] did not confirm this unusually short C–C bond but gave the following results: C–C = 1.52–1.60 Å., C–F = 1.37–1.34 Å., and ∠FCF = 107.5–109.5°.

The large discrepancy between these results suggested the present investigation of the structure of hexafluoroethane. It seemed that the earlier work might be improved upon in two ways: first, by obtaining diffraction patterns extending to larger scattering angles and, second, by a careful consideration of the vibrational and rotational effects within the molecule. These latter effects have often been neglected in electron diffraction studies.

## Experimental

The sample of hexafluoroethane (b.p. −76.2°) was supplied by the Central Research Department of the Minnesota Mining and Manufacturing Company; infrared spectroscopy indicated the sample to be better than 99% pure. Electron diffraction photographs were prepared in the customary manner[4] using an apparatus built by Dr. H. J. Yearian of the Purdue Physics Department. The camera distance was about 10.7 cm. and the wave length of the electron beam, as determined from transmission pattern of ZnO, was about 0.055 Å. The recorded diffraction pattern for hexafluoroethane extended to a $q$ value of about 105.

## Interpretation of the Pattern

The visual correlation method[4,5] and the radial distribution method[6,7] were used in the interpretation of the recorded pattern. The radial distribution function was calculated from the equation[7]

$$rD(r) = \sum_{q=1,2}^{q_{\max}} I(q) \exp\left(-bq^2\right) \sin\left(\frac{\pi q r}{10}\right) \qquad (1)$$

by the use of punched cards.[7] $I(q)$ is the visual intensity curve (curve vis., Fig. 2) which is drawn assuming no falling off of intensity with increasing $q$. The constant $b$ was chosen so that $\exp(-bq^2) = 0.10$ at $q = 105$. The terms for the range $q = 1$ to $q = 20$ were obtained from one of the acceptable theoretical intensity curves which were calculated on I.B.M. machines, using the equation[7]

$$I(q) = \sum_i \sum_j \frac{Z_iZ_j}{r_{ij}} \exp\left(-b_{ij}q_2\right) \sin\left(\frac{\pi q}{10} r_{ij}\right) \qquad (2)$$

All measurements and intensity estimates were made by three independent observers. The averages of the measurements of the three observers led to the $q_0$ values which are given in Table I.

Theoretical intensity curves were calculated over much of the parameter field indicated in Fig. 1 for rigid models of hexafluoroethane in which the symmetry of the point group $D_{3d}$ was assumed. Curve

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[1] Contains material from the Ph.D. thesis of James L. Brandt, Purdue Research Foundation Fellow in Chemistry, 1951–1952.

[2] A survey of electron diffraction results through 1949 is found in the tabulation by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[3] This value is quite accurate and is based on a combination of electron diffraction and infrared spectroscopic data made by K. Hedberg and V. Schomaker, THIS JOURNAL, **73**, 1482 (1951).

[4] L. O. Brockway, *Revs. Modern Phys.*, **8**, 231 (1936).

[5] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[6] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

[7] P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

TABLE I

$q/q_0$ VALUES OF ACCEPTABLE MODELS FOR HEXAFLUOROETHANE

| Feature Max. | Feature Min. | $q_0$ | P | R | S | X | Y | Z | CC | DD |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 19.45 | (0.961) | (0.951) | (0.941) | (0.987) | (0.967) | (0.967) | (0.998) | (0.998) |
| | 2 | 26.46 | .971 | .954 | .939 | .996 | .981 | .968 | 1.005 | 1.002 |
| 2 | | 30.12 | .990 | .976 | .965 | 1.013 | 1.005 | .988 | 1.023 | 1.021 |
| | 3 | 33.91 | .979 | .951 | .956 | 0.997 | 0.991 | .979 | 1.012 | 1.003 |
| 3 | | 37.79 | .961 | .946 | .941 | .986 | .973 | .966 | 0.996 | 0.990 |
| | 4 | 43.10 | .963 | .969 | .940 | .987 | .977 | .963 | 1.010 | .992 |
| 4 | | 47.77 | (.970) | (.957) | (.945) | (1.000) | (.984) | (.971) | (1.013) | (.994) |
| | 5 | 55.73 | (.976) | (.965) | (.956) | (1.002) | (.994) | (.984) | (1.020) | (1.014) |
| 5 | | 59.40 | .983 | .970 | .964 | 1.007 | 1.000 | .989 | 1.020 | 1.012 |
| | 6 | 62.91 | .976 | .960 | .942 | 0.997 | 0.981 | .966 | 1.007 | 0.994 |
| 6 | | 66.96 | (.993) | (.956) | (.931) | (1.012) | (.993) | (.963) | (1.023) | (1.008) |
| | 7 | 72.81 | .979 | .966 | .948 | 1.000 | .989 | .975 | 1.014 | 1.003 |
| 7 | | 77.46 | .984 | .969 | .949 | 1.009 | .991 | .975 | 1.028 | 1.002 |
| | 8 | 82.61 | .990 | .978 | .972 | 1.012 | 1.003 | .995 | 1.026 | 1.016 |
| 8 | | 86.69 | .982 | .972 | .962 | 1.004 | 0.994 | .981 | 1.016 | 1.007 |
| | 9 | 90.62 | .976 | .965 | .953 | 1.000 | .988 | .975 | 1.013 | 0.999 |
| 9 | | 94.86 | .985 | .948 | .956 | 1.005 | .995 | .980 | 1.014 | 1.004 |
| | 10 | 99.75 | .988 | .977 | .965 | 1.012 | 1.001 | .988 | 1.024 | 1.011 |
| 10 | | 104.15 | .986 | .975 | .963 | 1.010 | 0.999 | .986 | 1.020 | 1.012 |
| Av. (15 features) | | | 0.980 | 0.965 | 0.954 | 1.002 | 0.991 | 0.978 | 1.015 | 1.005 |
| Mean dev. | | | ±0.007 | ±0.009 | ±0.009 | ±0.007 | ±0.008 | ±0.008 | ±0.007 | ±0.007 |

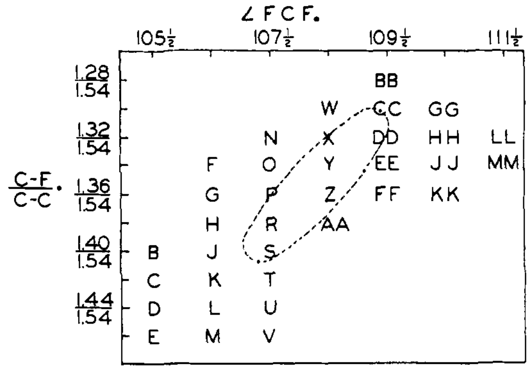

Fig. 1.—Parameters of models for which intensity curves were calculated. The dotted line indicates the limits of uncertainty in choosing the final model.

A of Fig. 2 represents the best of the rigid models and it may be rejected because of the well-resolved maximum rather than a shelf on the outer portion of the fourth maximum and because of the presence of a shelf on the inner portion of the ninth maximum. The parameters for Model A were C–C = 1.54 Å., C–F = 1.34 Å., and ∠FCF = 109.5°.

The failure of all rigid models to produce a suitable theoretical intensity curve indicated the importance of taking into account the intramolecular motions of the atoms. The problem of the effect of restricted internal rotation on the electron diffraction pattern has been discussed by Karle.[8] Adoption of Karle's expressions for use with the I.B.M. punched card method[7] permitted calculations for models corresponding to different potential barriers hindering the rotation of one $CF_3$ group with respect to the other. Models were then calculated for the parameters shown in Fig. 1 using a potential barrier of 5.0 kcal./mole; a description of agreement of the curves for these models follows.

Curves S and Z are shown in Fig. 2 as representa-

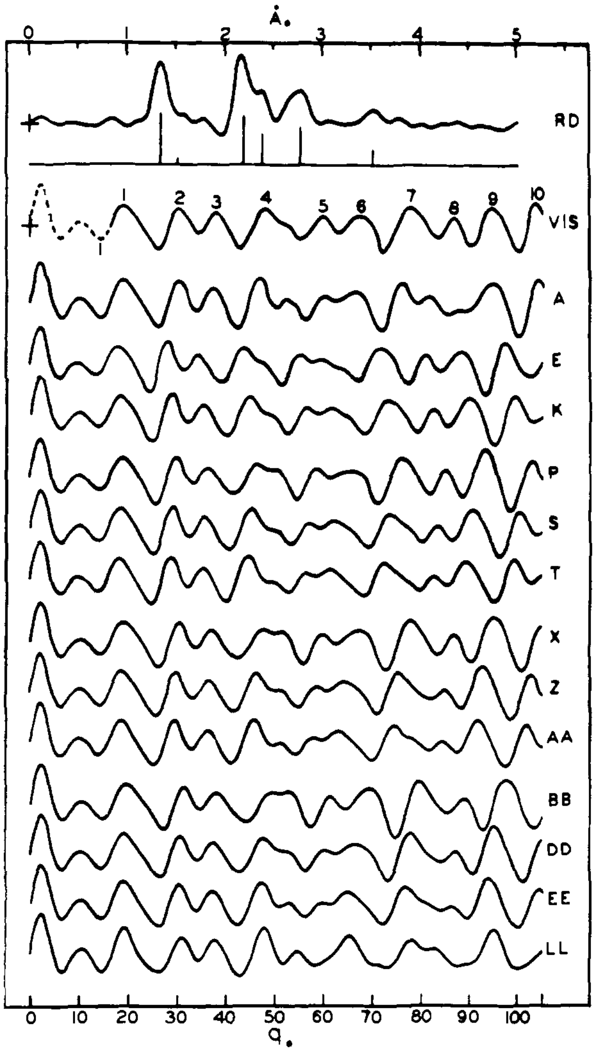

Fig. 2.—Radial distribution and intensity curves.

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(8) J. Karle, *J. Chem. Phys.*, **15**, 202 (1947).

tive of the entirely acceptable models which are enclosed by the dotted lines in Fig. 1. The area of acceptability indicates that the ∠FCF is about 108°.

Models with an ∠FCF of 105.5 or 106.5° such as E or K, give rise to curves which disagree completely with the visual curve in the shape of the sixth maximum. In addition, the relative depths of the ninth and tenth minima are wrong in the curves for these models. Curves corresponding to models with an ∠FCF of 110.5 or 111.5° are completely incompatible with the visual curve as seen by curve LL or by a curve intermediate between EE and LL.

Curves for models which lie above or on the dotted line in Fig. 1 were rejected or considered borderline for the following reasons: curve P, which is borderline at best, shows the fourth peak as an unresolved doublet rather than a peak with a shoulder on its outer portion; curves N and O are worse in this respect. Curve X is similar to P and is thus accepted as a borderline fit while W and BB are rejected for the same reasons as N and O. Models CC and DD are better as regards the fourth maximum but are considered borderline fits because the sixth maximum is too intense relative to the fifth.

Curves T, AA and EE, corresponding to models below the acceptable area in Fig. 1, are rejected largely on the basis of the appearance of the sixth and seventh maxima.

Table I summarizes the $q_{\text{calc}}/q_{\text{obs}}$ values for the acceptable or borderline models. The ratios for certain features are enclosed in parentheses; these were thought to be unreliable and were not used in calculating the $q/q_0$ averages.

The effects of different potential barriers are illustrated in Fig. 3 where curves $Y_3$, $Y_5$ and $Y_7$ correspond to model Y of Fig. 1 with potential barriers of 3.0, 5.0 and 7.0 kcal./mole, respectively. It is noted that as the barrier hindering free rotation is increased, *i.e.*, as the molecule is made more rigid, the shelf on the outer portion of maximum four becomes more pronounced and the intensity of the sixth maximum increases relative to the fifth maximum. From these curves and similar curves for models with other interatomic distances, it was concluded that the barrier is about 4 kcal./mole.

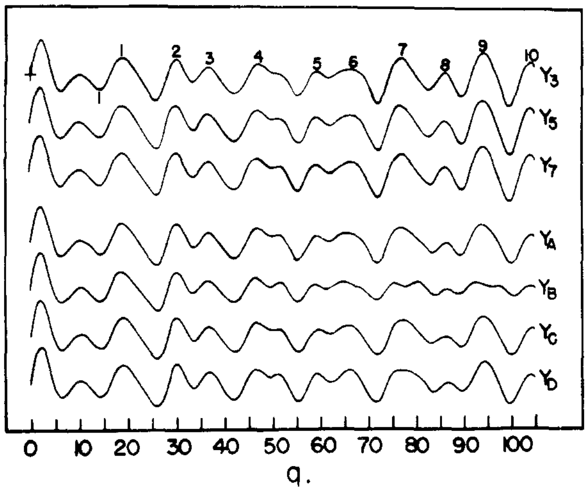

Fig. 3.—Theoretical intensity curves showing the effect of various barrier heights and different vibration factors.

In the above calculations, no account was taken of vibrational motion of the atoms; the models were rigid except for the restricted rotation of the $CF_3$ groups about the C–C axis. Curves $Y_A$ to $Y_D$ of Fig. 3 were calculated using in equation 2 the values of $b_{ij}$ given in Table II. The value of $28 \times 10^{-5}$ for the *gauche* F...F distance corresponds, to a very good approximation, to a potential barrier of 5.0 kcal./mole while the value $9.3 \times 10^{-5}$ is for a model which is nearly rigid with respect to internal rotation. The *trans* F...F distance is much less affected by restricted internal rotation and the values of $r_{ij} = 10.0 \times 10^{-5}$ for this distance allow for fairly large amplitudes of vibration affecting this distance. The remaining factors in model $Y_A$ are taken from those used to represent the vibrations in trifluoromethylacetylene.[9] The values in model $Y_B$ are adapted from those found for tetrafluoroethylene.[10] Model $Y_C$ differs from model $Y_A$ only in the magnitude of the damping factor for the *trans* F...F distance.

TABLE II

VALUES OF $b_{ij}$ USED FOR HEXAFLUOROETHANE MODELS

| Model distance | $Y_A$ $b_{ij} \times 10^5$ | $Y_B$ $b_{ij} \times 10^5$ | $Y_C$ $b_{ij} \times 10^5$ | $Y_D$ $b_{ij} \times 10^5$ |
|---|---|---|---|---|
| C–C | 0 | 0 | 0 | 0 |
| C–F | 1.5 | 11.5 | 1.5 | 1.5 |
| C...F | 9.0 | 41.9 | 9.0 | 9.0 |
| F...F | 6.8 | 34.6 | 6.8 | 6.8 |
| F...F (*gauche*) | 28.0 | 28.0 | 28.0 | 9.3 |
| F...F (*trans*) | 1.0 | 1.0 | 10.0 | 10.0 |

In curve $Y_A$ the shelf on the fourth maximum is slightly more intense than in curve $Y_5$ with which it is to be compared; otherwise these curves are in good agreement. The factors used in $Y_B$ are seen to be far too severe while $Y_C$ is seen to be in good agreement with $Y_5$. Curve $Y_D$ is clearly not in agreement with $Y_5$.

The conclusion from these and similar curves for other models in Fig. 1 is that the motion due to restricted internal rotation is much more important for the electron diffraction study than is the usual vibrational motion. So long as reasonable values of vibration factors are used (*e.g.*, those in models $Y_A$ and $Y_C$), the curves are virtually the same as for models in which only the internal rotation is taken into account. Thus it seems that no damping factors are necessary for the bonded and nonbonded C–F and the short F–F distances; the final results of this investigation (Table III) are based on models in which no damping was applied to these distances.

## Discussion of Results

Table III lists the values which are obtained from the various acceptable and borderline models after multiplying by the $q/q_0$ ratios. Also listed are the final values together with the radial distribution results (R.D.). These latter results are based on strong radial distribution peaks at 1.33,

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(9) J. N. Schoolery, R. G. Shulman, W. F. Sheehan, V. Schomaker and D. M. Yost, *J. Chem. Phys.*, **19**, 364 (1951).

(10) I. L. Karle and J. Karle, *ibid.*, **18**, 957 (1950).

TABLE III

DISTANCES (IN Å.) OBTAINED FROM $q/q_0$ VALUES

| | Model | | | | | | | | Final results with limits of acceptability | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Distance for | P | R | S | X | Y | Z | CC | DD | Final values | R.D. | |
| C–F | 1.333 | 1.332 | 1.336 | 1.322 | 1.328 | 1.330 | 1.319 | 1.326 | 1.330 ± 0.015 | 1.33 | |
| C–C | 1.509 | 1.487 | 1.469 | 1.543 | 1.526 | 1.506 | 1.563 | 1.547 | 1.51 ± .06 | | 1.53[a] |
| F...F | 2.146 | 2.142 | 2.156 | 2.144 | 2.150 | 2.160 | 2.151 | 2.160 | 2.15 ± .02 | 2.16 | |
| C...F | 2.351 | 2.335 | 2.318 | 2.353 | 2.348 | 2.337 | 2.353 | 2.350 | 2.34 ± .03 | 2.35 | |
| F...F (*gauche*) | 2.772 | 2.759 | 2.747 | 2.762 | 2.754 | 2.737 | 2.737 | 2.732 | 2.76 ± .03 | 2.76 | 2.75[a] |
| F...F (*trans*) | 3.507 | 3.492 | 3.491 | 3.495 | 3.497 | 3.480 | 3.490 | 3.486 | 3.49 ± .02 | 3.51 | 3.50[a] |
| ∠FCF | 107.5° | 107.5° | 107.5° | 108.5° | 108.5° | 108.5° | 109.5° | 109.5° | 108° ± 1.5° | | |

[a] Calculated from the three prominent peaks in the R.D. curve at 1.33, 2.16 and 2.35 Å.

2.16 and 2.35 Å. and less intense (and less reliable) peaks at 2.76 and 3.51 Å.

The C–C distance of 1.51 ± 0.06 Å. obtained in this investigation is intermediate between that obtained in the two previous investigations[2] and is believed to be more reliable than either of the previous results. The bonded C–F distance is more accurately determined than the C–C distance and is given here as 1.330 ± 0.015 Å. which is somewhat shorter than that reported in the previous investigations. Finally, the FCF angle is essentially in agreement with the previous results.

The results of this investigation do not make it possible to say with certainty whether the C–C distance in hexafluoroethane is the same as that in ethane; it is probable, however, that this distance is very nearly the same in the two compounds. The structure of the $CF_3$ group in $C_2F_6$ may be compared with the structure of this group in several other compounds. In the case of $CHF_3$, a recent electron diffraction investigation[11] by the rotating sector method gave C–F = 1.334 ± 0.005 Å. and ∠FCF = 108°30′ ± 30′ which agree well with microwave results[12] of 1.332 Å. and 108°48′, respectively. A microwave investigation[13] of $CF_3Br$ yielded C–F = 1.33 ± 0.015 Å. with ∠FCF assumed to be 108 ± 1°. In the case of $F_3CC{\equiv}CCF_3$, an electron diffraction study[14] indicated a C–F distance of 1.340 ± 0.020 Å. with ∠FCF = 107.5 ± 1°. An investigation of the structure of $HC{\equiv}CCF_3$ by a combination of electron diffraction and microwave methods[9] gave C–F = 1.335 ± 0.01 Å. and ∠FCF = 107.5 ± 1°. It is noteworthy that in all these cases the C–F distance is very nearly the same and that the FCF angle is less than the tetrahedral value.

**Acknowledgments.**—The authors wish to thank Professor Yearian for the use of his electron diffraction apparatus and Dr. Pearlson for the sample of $C_2F_6$. They are also grateful to the Purdue Research Foundation for financial support of this work.

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[11] L. O. Brockway, private communication.

[12] S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952).

[13] J. Sheridan and W. Gordy, *ibid.*, **20**, 591 (1952).

[14] W. F. Sheehan and V. Schomaker, THIS JOURNAL, **74**, 4468 (1952).

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

# Tracer Studies on the Decomposition of Ozone in Water

BY OTTO L. FORCHHEIMER AND H. TAUBE

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The direct exchange of $O_3$ with water in acid solution is very slow; however, exchange does take place to a limited extent when decomposition occurs. The exchange induced on decomposition is inhibited by $Cl^-$, HOAc and $HNO_3$ (at high concentration), but is the same in dilute $HClO_4$, $HNO_3$ or $H_2SO_4$ solution, and is the same for the hydrogen peroxide induced and the spontaneous decomposition. The extent of exchange increases as $O_3$ concentration decreases, to a value equivalent to the exchange of $^1/_6$ of the oxygen of the ozone decomposed. These results, in particular the extent of exchange, demonstrate hydroxyl radical as the exchange and decomposition active intermediate for the non-inhibited reactions. In alkaline solution, the exchange of ozonized oxygen and water under some conditions is greater than can be accounted for by the exchange of all the ozone decomposed; ozone catalyzes or induces the exchange of $O_2$ with water in alkali.

The hydroxyl radical has been proposed as an intermediate in a great variety of reactions in water solution.[1] While it is likely that this species is actually involved in many of the systems, in no case has proof been advanced that the intermediate carrying the bulk of the reaction is really the hydroxyl radical. The ubiquitous nature of the radical derives from the simple chemistry relating it to water, hydrogen peroxide and ozone, the difficulty of characterizing it from its high reactivity. It apparently reacts with a wide variety of substances, whether reagents or impurities in them, and even with rather inert reducing agents such as $Cl^-$ and HOAc.[2] The general ambiguity about mechanisms involving it centers around the question of whether a particular powerful oxidizing intermediate under study is the hydroxyl radical, or an intermediate generated by the reaction of hydroxyl radical with some substance in the solution. Thus in the work on the decomposition of ozone induced

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[1] N. Uri, *Chem. Revs.*, **50**, 375 (1952).

[2] H. Taube and W. C. Bray, THIS JOURNAL, **62**, 3357 (1940).