[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

The Mechanisms of Hydrogen Peroxide Reactions. I. The Conversion of Benzonitrile to Benzamide

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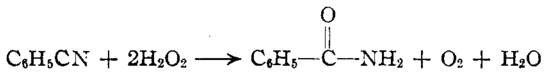
The rate of reaction between hydrogen peroxide and benzonitrile shows a first-order dependence on the concentration of the nitrile, hydrogen peroxide and hydroxyl ion. Benzonitrile oxide has been shown not to be an intermediate in the reaction, and the oxygen introduced into the nitrile has been demonstrated to arise from hydrogen peroxide and not from water or hydroxyl ion. The effect of substituents on the rate of the reaction parallels that observed in nucleophilic attacks on the carbon of the nitrile. These data suggest that the first step is a reaction between the nitrile and peroxide anion, followed by a fast reaction with a molecule of hydrogen peroxide. The peroxide anion appears to be a particularly effective nucleophilic agent in its reaction with benzonitrile.

Introduction

Hydrogen peroxide is an unusual reagent in that it is known to function both as an oxidizing agent and as a reducing agent. Although many examples of both types of reactions are known, little has been done in an effort to elucidate the mechanisms of these transformations. A particularly interesting example is the reaction of an aromatic nitrile with hydrogen peroxide in weakly basic solution.[1] The stoichiometry of the reaction suggests that it effectively involves an oxidation–reduction of hydrogen peroxide with simultaneous hydration of the nitrile.



$$C_6H_5CN + 2H_2O_2 \longrightarrow C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + O_2 + H_2O$$

It was believed that an examination of the kinetics and other pertinent data concerning this reaction would lead to the formulation of a mechanism for the reaction, and also might give one an insight into the nature of the other reactions of hydrogen peroxide.

Experimental

The example chosen for study was the reaction of benzonitrile with hydrogen peroxide in buffered aqueous acetone solution at 40°. This temperature was chosen because the decomposition of hydrogen peroxide is fairly slow under these conditions.[2] In order to obtain a sufficiently high concentration of the nitrile, it was found necessary to add an organic solvent. Acetone, ethanol, dioxane and tetrahydrofuran were considered as possible solvents. Acetone was chosen since hydrogen peroxide showed a lower rate of decomposition in 25% acetone than in mixtures of the other solvents with water. Acetone–water has been used with success as a solvent for this reaction.[1]

Since it is known that the reaction is base catalyzed,[1] it was necessary to use a buffer in order to control the *p*H. It was observed that the addition of hydrogen peroxide to the borate buffer used, caused a decrease in *p*H in excess of that due to the sulfuric acid present as a stabilizer in the hydrogen peroxide. It is known[3] that boric acid reacts with hydrogen peroxide to form perboric acid which is a stronger acid than boric acid. However, the equilibrium constant for the reaction is very small, indicating the presence of only a small quantity of perboric acid in the reaction mixtures. The amount of hydrogen peroxide removed from solution by this reaction was estimated to be less than 5% for most of the runs. A similar effect was noted when a phosphate buffer was used, although it was of a smaller magnitude.

Reagents.—Benzonitrile was a purified Eastman Kodak Co. white label grade. The other nitriles were obtained from the same source. Acetone was a C.P. grade which was inert to neutral potassium permanganate. Hydrogen peroxide was a C.P. grade of 3% strength, the same lot being used for all the experiments.

The boric acid solution (0.82 *M*) was prepared by cooling a saturated aqueous solution to 20° for two hours, followed by filtration. The sodium hydroxide solution was 0.100 *N*, prepared carbonate free. The sodium thiosulfate solution (0.1 *N*) was used within a week after its preparation.

Analytical Method.—The rate of reaction was followed by measuring the rate of disappearance of hydrogen peroxide. Ten milliliter aliquots were removed from the reaction flask and added to a solution of two grams of potassium iodide and 10 ml. of 18 *N* sulfuric acid in 125 ml. of water. The liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution. Under these conditions, neither acetone nor oxygen interfered with the analysis.

The *p*H of the solutions was determined using a Beckman model G *p*H meter. It was noted that an 0.001 *N* solution of sodium hydroxide in 25% acetone gave an observed *p*H of 11.4. The *p*H values determined in this solvent are therefore approximately 0.4 *p*H unit high.

Kinetic Method.—One hundred milliliters of an acetone solution containing four times the desired quantity of the nitrile was prepared. Ten milliliters of 0.82 *M* boric acid solution, the necessary amount (5, 10 or 20 ml.) of 0.1 *N* sodium hydroxide solution for the desired *p*H, 25 ml. of the nitrile solution and 20 ml. of distilled water were mixed in a 100-ml. volumetric flask and allowed to warm in a thermostat maintained at 40.0°. The desired amount of hydrogen peroxide solution (10 or 20 ml.) which had been warmed to 40° was added at zero time, and sufficient 40° water was added to make 100 ml. The reaction flasks were wrapped in aluminum foil in order to minimize photochemical decomposition of the peroxide. Most of the runs were made in duplicate, the results thus obtained being in very good agreement. The reactions were carried to 20–50% completion.

Blank runs were made simultaneously with each rate determination in order to estimate the extent of self decomposition of the hydrogen peroxide. This reaction was about one-seventh as fast as the nitrile reaction, and was corrected for in calculating the rate constants. The rate constants given are in effect based on the rate of appearance of product and were calculated using the natural logarithm. The probable error in the rate constants was estimated to be about 10%.

It was not possible to use 25% acetone as the solvent for the reaction of the substituted benzonitriles because of their limited solubility. Therefore, 50% acetone was employed. The method used was the same as above, except that 50 ml. of an acetone solution and correspondingly less water was used.

The Reaction of Benzonitrile with Hydrogen Peroxide.—Benzonitrile oxide was prepared by the method of Wieland[4] from benzhydroxamyl chloride and dilute base. It was used immediately in order to avoid polymerization. To a mixture of 1.5 ml. of 20% hydrogen peroxide and 5 ml. of water was added 0.8 g. of benzonitrile oxide and sufficient acetone to effect solution. After the addition of 3 ml. of 10% sodium carbonate solution, the mixture was allowed to stand overnight. The acetone and water were removed by evaporation on a steam-bath. The infrared absorption spectrum of the product (in acetonitrile solution) was com-

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[1] B. Radziszewski, *Ber.*, **17**, 1289 (1884); L. McMaster and C. R. Noller, *J. Ind. Chem. Soc.*, **12**, 652 (1935); J. V. Murray and J. B. Cloke, THIS JOURNAL, **56**, 2749 (1934).

[2] Fr. Bürki and Fr. Schaft, *Helv. Chim. Acta*, **4**, 418 (1921).

[3] H. Menzel, *Z. physik. Chem.*, **105**, 402 (1923).

[4] H. Wieland, *Ber.*, **40**, 1670 (1907).

pared with that of benzamide, and indicated the absence of a significant amount of the latter. The product was found not to melt under 250°, and on heating on a spatula, melted, charred and emitted a lachrymatory vapor. Under these conditions, using twice the quantity of hydrogen peroxide, benzonitrile gave a quantitative yield of benzamide.

The Reaction of Benzonitrile with Hydrogen Peroxide and H_2O^{18}.—To a mixture of 1 ml. of 90% hydrogen peroxide and 5 ml. of water containing 1.4% H_2O^{18} was added 1 g. of benzonitrile and sufficient acetone to effect solution.[5] After the addition of 3 ml. of 10% sodium carbonate solution, an exothermic reaction occurred and oxygen was evolved. After standing overnight, the solvents were removed by evaporation, and the product was washed with cold water and dried.

The product was analyzed for its O^{18} content by passing its vapor, mixed with nitrogen, through a tube containing granular quartz heated to 425°.[6] The benzonitrile and water formed were collected in a small trap and equilibrated with carbon dioxide overnight. Analysis of the carbon dioxide using a mass spectrometer indicated that the amide contained 0.030% O^{18} over normal abundance.[7]

Results

The results of a typical kinetic run are shown in Table I. These results clearly indicate the reaction to be of the second order. The increase in k with time can be attributed to the small increase in pH as the hydrogen peroxide concentration decreased. A more significant conclusion may be reached on the basis of the data in Table II. In this case the rate constants were derived from the initial rate of the reaction in order to avoid errors caused by a change of pH during the reaction. In all cases, the rate constants were calculated for a considerable proportion of the reaction, with results similar to those shown in Table I.

TABLE I

Solvent, 25% acetone (by volume); temp., 40.0°; $[H_2O_2] = 0.180$; $[C_6H_5CN] = 0.090$; pH 7.58.

Time	Reaction of H_2O_2, %	Reaction of C_6H_5CN,[a] %	$k \times 10^5$ 2nd order
30	1.4	1.2	3.8
60	2.8	2.4	3.8
120	5.2	4.3	3.5
240	10.9	9.5	4.0
300	13.0	11.2	4.0
450	19.7	17.0	4.3
1380	43.8	39.5	4.5

[a] Calculated from the rate of disappearance of hydrogen peroxide from the reaction mixture, and an independent blank.

A comparison of runs 1 and 2 indicates that the borate buffer did not enter into the reaction, since the rate was essentially the same when the buffer concentration was doubled. Runs 1, 3 and 4 indicate the reaction to be first order in both hydrogen peroxide and in benzonitrile, since halving the concentration of either compound resulted in no significant change in the second-order rate constant. Runs 1, 5 and 6 showed the rate of reaction to be proportional to the concentration of hydroxyl ion within experimental error. Run 7, in which a phosphate buffer was used, gave essentially the same observed rate constant as run 5, indicating again that the buffer did not enter into the reaction. Finally, run 8 was carried out in 25% ethanol, by volume, instead of 25% acetone, and gave qualitatively the same rate as run 5 which had the same pH. This indicated that the solvent acetone did not enter into the reaction. The third order rate constants listed in the last column are based on the observed pH value which is about 0.4 pH unit high. Thus, these values of k should be multiplied by a factor of 2.5 to obtain the actual rate constants.

TABLE II

Solvent, 25% acetone; temp., 40.0°.

Run no.	$[H_2O_2]$	$[C_6H_5CN]$	pH[a]	0.1 N NaOH,[b] ml.	0.82 M H_3BO_3,[b] ml.	$k \times 10^5$[c] 2nd order	$k \times 10^1$[d] 3rd order
1	0.180	0.090	7.58	10	10	3.9	5.1
2	.180	.090	7.58	20	20	3.7	4.9
3	.092	.090	7.58	5	10	3.8	5.0
4	.184	.045	7.58	10	10	4.0	5.3
5	.181	.090	8.07	20	10	12.3	5.2
6	.183	.090	7.19	5	10	1.47	4.8
7	.181	.090	8.06	[f]	[f]	11.2	4.8
8[e]	.182	.090	8.08	10	10	16.3	...

[a] The observed pH values in this solvent are approximately 0.4 pH unit high. The observed values are listed in this table. [b] Volume per 100 ml. of reaction solution. [c] Observed rate constant: $-d[H_2O_2]/dt = 2k[H_2O_2][RCN]$; units, 1 mole^{-1}sec.$^{-1}$. [d] Calculated rate constant: $-d[H_2O_2]/dt = 2k(K_a/K_w)[H_2O_2][RCN][HO^-]$; $K_a = 2 \times 10^{-12}$. [e] 25% ethanol was employed for this run. [f] 10 ml. of 1.0 N Na_2HPO_4 and 2 ml. of 0.5 N HCl were used per 100 ml. of reaction mixture.

The results of an investigation of the effect of substituents on the rate of the reaction are shown in Table III. The introduction of a chloro group increased the rate, and the effect of a nitro group was observed to be considerably greater. These reactions were carried out in 50% acetone rather than 25% acetone because of the limited solubility of the substituted compounds. It may be noted that the rate constant in 50% acetone was 3.6 × 10^{-5} l. mole^{-1} sec.$^{-1}$ at a corrected pH of 7.4, and in 25% acetone it was 3.9 × 10^{-5} at a corrected pH of 7.2. The effect of changing dielectric constant is therefore small.

TABLE III

Solvent, 50% acetone; $[H_2O_2] = 0.180$; temp., 40.0°

Run no.	Compound	Concn.	pH[a]	$k \times 10^5$[b] 2nd order
9	Benzonitrile	0.090	8.60	3.6
10	p-Chlorobenzonitrile	.090	8.60	15
11	p-Nitrobenzonitrile	.050	8.60	85

[a] Swain and Scott, THIS JOURNAL, 75, 141 (1953), have indicated that the observed pH values in 50% acetone are high by about 1.2 pH units. The table gives observed pH values. [b] See note c, above.

In order to obtain some information concerning this reaction, other than rate data, the conversion of benzonitrile to benzamide was carried out in the presence of H_2O^{18}.[8] Pyrolysis of the benzamide followed by analysis of the water gave a value of 0.030% excess O^{18} over normal abundance. A

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(5) This is essentially the procedure suggested by Murray and Cloke, ref. 1.

(6) R. S. Boehner and A. L. Ward, THIS JOURNAL, **38**, 2506 (1916), found that benzamide was almost quantitatively converted to benzonitrile and water under these conditions. The products obtained in the first run were discarded in order to prevent dilution of the product water with residual water in the cracking catalysts.

(7) The O^{18} content was kindly determined by Mr. R. Wade using a Consolidated Engineering Corp. Model 21-201 mass spectrometer.

(8) Obtained from the Stuart Oxygen Co., under allocation from the Atomic Energy Commission.

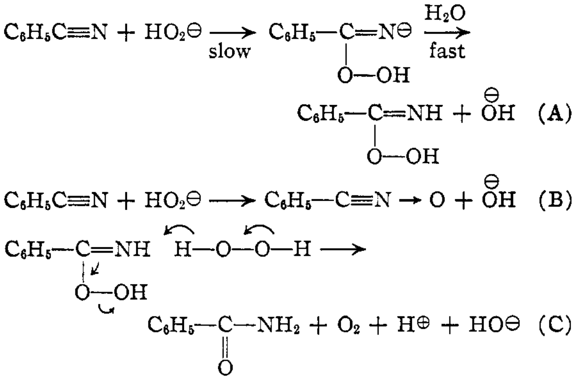
value of 0.6–0.7% would be expected if the oxygen arose from water or hydroxyl ion instead of hydrogen peroxide.

In order to determine if benzonitrile oxide could be an intermediate in this reaction, the oxide was treated with hydrogen peroxide under conditions which led to a quantitative conversion of benzonitrile to benzamide. The product of the reaction was a high melting, unidentified solid which appeared to contain little if any benzamide.

Discussion

Since the rate of the reaction showed a first-order dependence on the concentration of hydrogen peroxide, the slow step must involve only one molecule of the peroxide, and a successive fast reaction must be responsible for the second hydrogen peroxide molecule required by the stoichiometry. The rate expression suggests that either hydroxyl ion and hydrogen peroxide react independently with the nitrile, or peroxide anion alone reacts with the nitrile in the slow step. The first possibility is very unlikely since the attack of hydroxyl ion on the nitrile would be expected to lead to simple hydrolysis without the participation of hydrogen peroxide.

If peroxide anion is assumed to be the reacting species, it can react with the nitrile either at the carbon (A) or at the nitrogen (B). The intermediate I could then react with a molecule of hydrogen peroxide (C) to give the amide. It is not equally apparent how the nitrile oxide might give the amide. The fact that benzamide was not obtained from benzonitrile oxide makes reaction B appear unlikely. Reactions A and C then remain as a reasonable interpretation of the course of the reaction.



$$C_6H_5C{\equiv}N + HO_2^{\ominus} \xrightarrow[\text{slow}]{} C_6H_5{-}\underset{\substack{|\\ O{-}OH}}{C}{=}N^{\ominus} \xrightarrow[\text{fast}]{H_2O} C_6H_5{-}\underset{\substack{|\\ O{-}OH}}{C}{=}NH + \overset{\ominus}{O}H \quad (A)$$

$$C_6H_5C{\equiv}N + HO_2^{\ominus} \longrightarrow C_6H_5{-}C{\equiv}N \rightarrow O + \overset{\ominus}{O}H \quad (B)$$

$$C_6H_5{-}\underset{\substack{|\\ O{-}OH}}{C}{=}NH \quad H{-}O{-}O{-}H \longrightarrow C_6H_5{-}\underset{\substack{\|\\ O}}{C}{-}NH_2 + O_2 + H^{\oplus} + HO^{\ominus} \quad (C)$$

If the proposed mechanism is correct, the introduction of substituents into benzonitrile should result in a change of rate which would correspond to that observed in a nucleophilic attack on benzonitrile. Kindler,[9] in his study of the reaction of substituted benzonitriles with sulfhydryl ion, has shown that chloro and nitro groups accelerate the reaction in that order. The same order has been observed in the present case, lending further support to the proposed mechanism. Additional evidence may be found in the observation that the oxygen introduced into the nitrile during the reaction arose from hydrogen peroxide rather than from water or hydroxyl ion.

If the proposed mechanism may be considered to be established, a comparison of the rate of this reaction with other nucleophilic attacks on the carbon of the nitrile would be of interest. The available data are summarized in Table IV. It is apparent that peroxide anion is a particularly effective nucleophilic agent in its reaction with benzonitrile.

TABLE IV

Anion	Solvent	Temp., °C.	k, l. mole^{-1} sec.$^{-1}$	Ref.
HO_2^-	25% acetone	40	1	
HS^-	100% ethanol	69	$2–8 \times 10^{-2}$	10
EtO^-	100% ethanol	25	2×10^{-4}	11
HO^-	25% acetone	40	$\sim 1 \times 10^{-4}$	12

It is well known that sulfur containing anions have high nucleophilic reactivity, as compared to hydroxyl ion, in the S_N2 displacement reaction.[13] This reactivity is presumed to be a consequence of the higher polarizability of the sulfur, which will accommodate some of the extra electron density at the carbon in the transition state. It is also known that hydroxyl ion is particularly effective in its reaction with β-propiolactone,[14] this being due, at least in part, to the possibility of having the carbonyl oxygen bear the negative charge in the transition state.[13] Although the present reaction would appear to resemble the ester reaction more than the S_N2 displacement, a comparison with β-propiolactone is not fruitful since hydroxyl ion behaves differently in this reaction than do other ions.

Unfortunately, the reactions of ordinary esters or other acid derivatives with nucleophilic agents have been little studied. Although it is known that some esters and acid chlorides react with sulfhydryl ion to give thiol acids,[15] the rate of this reaction as compared to that of hydroxyl ion does not appear to have been measured. If sulfhydryl ion were more reactive than hydroxyl ion in this reaction, then the reactivity of peroxide anion might be explained by an argument similar to that for the sulfur containing anions. Although peroxide anions does not have the benefit of higher polarizability at the attacking atom, it does have the possibility of transferring part of the negative charge to the other oxygen. It is interesting to note that even though peroxide anion has a negative charge, it in effect transfers a *neutral* oxygen.

If, on the other hand, hydroxyl ion is more effective than sulfhydryl ion in its reaction with esters or acid chlorides, it would then be necessary to

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(9) K. Kindler, *Ann.*, **450**, 1 (1926).

(10) K. Kindler, ref. 9, gave a value of 9×10^{-3} l. mole^{-1} min.$^{-1}$ as the first-order rate constant for the reaction between benzonitrile and a constant concentration of sulhydryl ion. He unfortunately neglected to mention the concentration of sulfhydryl ion. From the experimental details, one may calculate that the HS^- concentration must have been between 0.01–0.002 *M*, depending upon the size of the volumetric flask he employed (50–250 ml.). This reaction will be reinvestigated.

(11) E. K. Marshall, Jr., J. P. Harrison and S. F. Acree, *Am. Chem. J.*, **49**, 400 (1913), have determined the rate of the reverse reaction and also the equilibrium constant. From these data, the rate of the forward reaction was calculated.

(12) Benzonitrile (0.1 *M*) and sodium hydroxide (0.1 *M*) in 25% acetone at 40° gave about 45% reaction in 22 hr. as determined by the ultraviolet absorption spectrum.

(13) *Cf.* C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

(14) P. D. Bartlett and G. Small, *ibid.*, **72**, 4867 (1950).

(15) A. Kekule, *Z. Chem.*, 196 (1867).

examine the reactions of nitriles in order to find an explanation for the high reactivity of both sulfhydryl ion and peroxide anion. Current work is directed toward a more detailed investigation of these points.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORIGA INSTITUTE OF TECHNOLOGY]

The Effect of Halogen Atoms on the Reactivity of Other Halogen Atoms in the Same Molecule. III. The S_N2 Reactivity of Ethylene Halides[1]

BY JACK HINE AND W. H. BRADER, JR.

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The interpretations of earlier data as showing that the replacement of β-hydrogen atoms in alkyl halides by halogen atoms causes increased S_N2 reactivity are shown to be unreliable. The kinetics of the bimolecular substitution reaction of sodium thiophenolate with ethyl bromide and five of its β-substituted derivatives have been studied. For the various β-substituents, the rates vary thus: $H > C_2H_5 \sim CH_3 > Cl \sim Br \sim F$. The heats of activation are found to increase with electron-withdrawing power of the substituents studied, while the entropies of activation decrease with increasing size.

The substitution of a β-hydrogen atom in an alkyl group by a halogen atom is commonly said[2] to increase the reactivity by the S_N2 or one-step bimolecular displacement mechanism.[3] The evidence quoted includes the data of Tronov and Gershevich,[4] who reported rate constants for the reaction of sodium methoxide with *n*-propyl bromide, isopropyl bromide, propylene bromide, trimethylene bromide, 1,2,3-tribromopropane and other halides of propane. From what is known of the chemistry of polyhalides of this type it might be expected that a major reaction with the strongly basic reagent sodium methoxide would be dehydrohalogenation.[5] Thus, the fractions of the rate constants obtained by these workers which are due to substitution reactions are not definitely known. The data of Slator, who studied the reactions of sodium thiosulfate with a number of halogen compounds,[6] have also been quoted in this connection. Slator indeed found that the second-order rate constant for the reaction with ethylene iodide is considerably greater than that for reaction with ethyl iodide, but no attention appears to have been called to his observation that ethylene bromide was considerably less reactive than ethyl bromide. Since we have now found that the reaction of ethylene iodide with sodium thiosulfate yields largely ethylene, it is clear that these data may not be used as the basis for generalizations concerning *displacement on carbon*.

It should also be noted that although Slator obtained reasonably steady first-order rate constants for the reaction of ethylene chlorobromide and chloroiodide with excess sodium thiosulfate, these are not the rate constants for first-order solvolysis, as has been suggested.[7] This follows from the fact that the rate constants for the solvolysis of these compounds are smaller by factors of more than one thousand than the constants reported by Slator,[8] as well as from inspection of some of Slator's data.[9] Although a second-order reaction in which rate "constants" climb (due to some replacement of the second halogen atom) could give reasonable first-order rate constants, we cannot be sure that this is being observed in the present case, since another side reaction, hydrolysis of the Bunte salt to a mercaptan and acid, was shown by Slator to be present and other reactions such as dehalogenation may also have been occurring.

From the data of Taylor[10] the rate of the second-order substitution reaction of ethanolic alkali with ethylene bromide may be calculated to be two or three times that for reaction with ethyl bromide, but this calculation depends on a difficult and not altogether satisfying analysis of the products of the former reaction.[11]

We have not been able to devise a method for determining accurately the effect of β-iodine atoms on S_N2 reactivity, since the nucleophilic reagents which have been studied attack the β-iodine atom

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[1] Papers I and II of this series: J. Hine and D. E. Lee, THIS JOURNAL, **73**, 22 (1951); **74**, 3182 (1952).

[2] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 89; M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 71; A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 394. E. D. Hughes and C. K. Ingold [*J. Chem. Soc.*, 244 (1935)], have also made a statement of this type, but in an article which has come to our attention since this investigation began [E. D. Hughes, *Quart. Revs.*, (*London*), **5**, 254 (1951)], it is recognized that none of the existent data unambiguously describe the rate of a substitution (in contrast to elimination) process and stated ". . . investigations of suitable systems are being undertaken."

[3] For the significance of the term S_N2, see I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946), and earlier papers.

[4] B. V. Tronov and A. I. Gershevich, *J. Russ. Phys. Chem. Soc.*, **59**, 727 (1927); *C. A.*, **22**, 3389^9 (1928).

[5] Sodium hydroxide and 1,2,3-tribromopropane give 2,3-dibromopropene in more than 80% yield (R. Lespieau and M. Bourguel, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 209). Ethylene bromide with sodium hydroxide in homogeneous aqueous dioxane solution gives more than 90% elimination (J. Hine and W. H. Brader, unpublished work).

[6] A. Slator, *J. Chem. Soc.*, **85**, 1286 (1904).

[7] L. P. Hammett, "Physical-Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 208. See also E. A. Moelwyn-Hughes, *Nature*, **133**, 294 (1934).

[8] J. Hine and W. H. Brader, unpublished work.

[9] The rate constants calculated as first order in ethylene chlorobromide increase with increasing thiosulfate concentration. The order of a reaction in which an excess of ethylene chloroiodide was used was reported to be about 1.85.

[10] W. Taylor, *J. Chem. Soc.*, 1514 (1935).

[11] The work of B. V. Tronov and L. V. Laduigina [*J. Russ. Phys. Chem. Soc.*, **62**, 2165 (1930); *C. A.*, **25**, 3957 (1931)], P. Petrenko-Kritchenko and V. Opotsky [*Ber.*, **59B**, 2131 (1926)] and many other data on reactions of nucleophilic reagents with 1,2-dihalides, also probably include large amounts of elimination as well as substitution reactions.