

neous idea of the amount of decomposition, it does not seem likely that pressure measurements will have a simple relationship to the amount of methyl propyl ketone decomposed in any part of the reaction.

Ethylene and propylene also react and decrease greatly in amount during the decomposition.^{4a} Since propylene inhibits the decomposition,^{4a} that effect will operate to increase the complexity of the process. As with methyl *n*-butyl ketone,³ one must conclude that a complete kinetic analysis of the free radical chain mechanism is not possible with the data available. However, the great similarity of the behaviors of these two ketones is apparent. It is seen that the chain steps above are

analogous to those advanced for methyl *n*-butyl ketone.³

It is likely that the carbon dioxide reported by Waring and Garik^{4a} is produced by the reactions of ketene since carbon dioxide is a major product of the ketene decomposition at these temperatures.¹⁷

Combining the analyses here with those of Waring and Garik,^{4a,7} one can see that, if the above steps 1-4 represent the decomposition, steps 2 and 3 are most important.

Acknowledgment.—The author wishes to acknowledge the many helpful comments of Dr. W. D. Walters who suggested this problem. The gaseous infrared analyses were performed by Mr. C. A. Whiteman.

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

The Exchange of Hypochlorite and of Hypobromite Ions with Water

BY M. ANBAR AND H. TAUBE

RECEIVED FEBRUARY 23, 1956

The reaction of ClO^- and BrO^- with NO_2^- proceeds with almost complete transfer of hypochlorite oxygen to nitrite. This reaction has been applied in the isotopic analysis of ClO^- and BrO^- undergoing exchange with water. The exchange of ClO^- and water in alkaline solution proceeds by the paths $k_A[(\text{ClO}^-)/(\text{OH}^-)]$ and $k_B[(\text{ClO}^-)(\text{Cl}^-)/(\text{OH}^-)]$. Paths of similar kinetic form are indicated for the exchange of BrO^- and water, and Cl^- as well as Br^- can catalyze the exchange. The reactions reverse to the k_B paths are the attack of Cl_2 , Br_2 or BrCl by OH^- , and the specific rates for these reactions have been calculated. The mechanisms of the reactions and the mode of action of H^+ in reactions of oxy-ions are discussed.

In the course of tracer work on the reactions of oxy-anions with nitrite ion in water, it was observed that when ClO^- or BrO^- are the oxidizing agents, almost complete transfer of oxygen to the reducing agent takes place. The reactions with nitrite provide a means of isotopic analysis of the hypochlorites and therefore of following the rate at which oxygen exchanges between them and water. While the method thus made available is far from ideal, the exchange reactions in question are of such interest in themselves, as well as for comparison with other substitution or oxidation-reduction reactions of the hypochlorites, that it was considered worthwhile to obtain even data of the quality of those reported in this paper. This decision was not reached without making an extensive survey¹ of other reactions which might be exploited for oxygen isotope sampling, but none was discovered superior to that adopted here. Some of the disadvantages of the present sampling method could be avoided by sampling the solvent by distillation. This method, however, is not accurate for dilute solutions of the solute.

Experimental

Reagents.—The hypochlorite solution was prepared by passing Cl_2 through ice-cooled 5 *M* NaOH , then gradually adding freshly prepared Ag_2CO_3 until Ag_2O , recognizable by its color, began to form. The solution at $\text{pH} > 13$ was stored in a refrigerator. The hypobromite was prepared in a similar manner, but because of the greater rate of decomposition, was used within 24 hr. Other chemicals were of A.R. quality, used without further purification.

Procedure.—Solutions in O^{18} -enriched water, each of total volume ca. 20 ml. were prepared, containing the hypochlorite as well as appropriate amounts of H_2SO_4 and NaH_2PO_4 and

kept in a thermostat. The adjustment of pH was made, using a Beckman pH meter, with a special electrode for alkaline solution. Measurements were reproducible to ca. 0.03 pH unit. Aliquots were withdrawn at intervals for isotopic assay of the hypochlorite. Each sample immediately after being withdrawn was mixed with enough sodium nitrite solution to leave the oxidizing agent in slight excess and then was added with stirring to 100 ml. of water buffered to a pH of 1. After reaction, which was found to be complete within 10 sec., H_2O_2 was added to remove the excess hypochlorite. Solid Ag_2SO_4 and $\text{Ba}(\text{OH})_2$ were now added, and the solution was adjusted to pH 9 using NaOH . After filtration, which removes sulfate, phosphate, halide and silver from the system, the pH of the solution was adjusted to between 5 and 6 with acetic acid, and nitron (diphenylenediaminehydrotriazole) reagent was added. The solution was left for about 12 hr. for crystallization of nitron nitrate. This was filtered off, digested with ammonium hydroxide and was reprecipitated. After digesting the precipitate again with ammonium hydroxide, the remaining nitron base was extracted with ethyl acetate. The solution was then evaporated to dryness, the final drying being done under vacuum. The N_2O for isotopic analysis was obtained by decomposition of the NH_4NO_3 comprising the residue, the gas first being purified by storage over solid NaOH .

In spite of pains to improve the method of isotopic analysis, specific rates calculated from results for successive aliquots of a given reaction mixture are found to differ by as much as a factor of 2. These fluctuations do not correspond to real changes in rate, since they follow no trend with time, and furthermore the data within a precision of a factor of 2 or so conform to a simple and reasonable rate law, over a very wide range in rate. It has been shown by direct experiments that the handling of the nitrate is not responsible for the fluctuations. The principal error seems to be incurred in the reaction of nitrite and hypochlorite, for the conditions necessary to make this reaction rapid also increase the rate of exchange between hypochlorite and water. Partial exchange intervenes from time to time. This causes an apparent reduction in the rate of exchange, because the environment during the quenching reaction has nearly the isotopic composition of the initial hypochlorite. To conform to this analysis, the theoretical line in Fig. 1 has been drawn through a high density of points corresponding to the higher

(1) The results of these tracer experiments will be described in a separate article.

rates of exchange. Positive deviations are still left, attributable to random errors in isotopic analysis, the measurement of pH and possibly to stray catalytic effects. In spite of the irreproducibility of the data, important conclusions can still be drawn from them, consisting as they do of a large number of determinations over a wide range of variation in some of the parameters to which the rate is sensitive.

Definitions and Conditions.—Specific rates were calculated from the results for individual aliquots. Since one of the exchanging forms, H_2O , is so much more abundant than the other, the specific rates calculated from the change in isotopic composition of the hypohalite are equivalent to the specific rates, first order in hypohalite, for total rate of the exchange reaction.

Lower case k is used for specific rate, modified by subscript if reserved to represent a particular reaction; upper case K is used for equilibrium quotients. Total hypohalite, whether X or HXO , is represented by the symbol $X(I)$. E represents the O^{18} -enrichment ratio of the N_2O in question, *i.e.*, the ratio N_2O^{18}/N_2O^{16} compared to that obtained for the reaction of isotopically normal XO^- corresponding to zero exchange, with the nitrate used for analysis.

Unless otherwise indicated, the units used are minutes for time and moles per liter for concentration.

All experiments were done at 25° .

Results

Table I contains a summary of the experiments on the transfer of oxygen from ClO^- to NO_2^- .

Exchange of NO_2^- or ClO^- with the solvent before reaction will decrease the apparent transfer. Thus the values in the last column of Table I are minimum values. The actual transfer may well be close to 100%, as indicated by experiment 1.04, the defect being caused by the exchange with water during the analysis.

The bulk of the results obtained on the exchange of ClO^- and water are not reported in detail but are entered in the graph of Fig. 1. Some of these experiments are summarized in Table II to illustrate the dependence of specific rate on the time of reaction and the concentration of ClO^- .

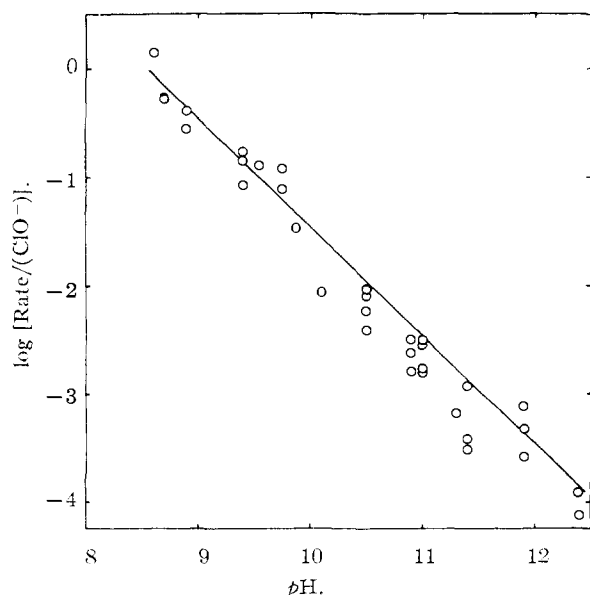


Fig. 1.—The specific rate of the exchange of ClO^- and water, as function of pH .

The exchange of ClO^- and water is strongly catalyzed by Cl^- . In Fig. 2 are shown the results of experiments devoted to studying this effect. The specific rates (divided by (Cl^-)) plotted as

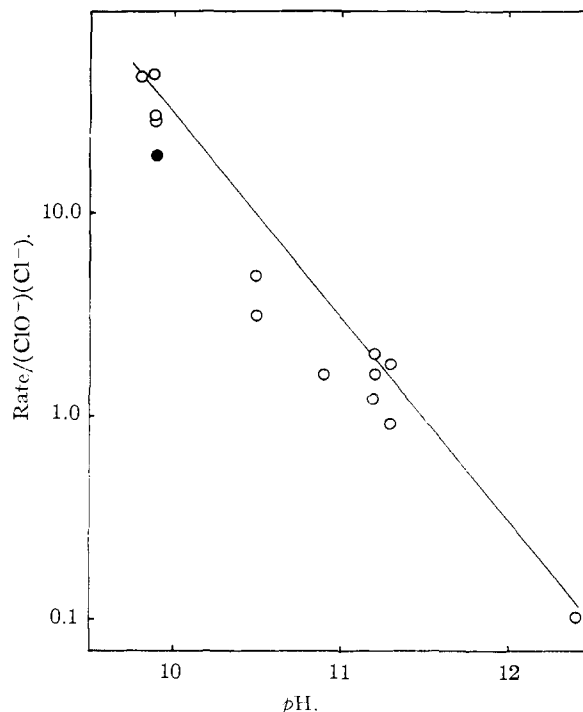


Fig. 2.—The specific rate of exchange of ClO^- and H_2O catalyzed by Cl^- , as function of pH .

ordinates were obtained by subtracting from those directly calculated the specific rate for the non-catalyzed path, as taken for the appropriate pH from the line in Fig. 1. In all but one experiment, the correction was less than 25% of the total. In

TABLE I

TRACER EXPERIMENTS ON THE REACTION OF NO_2^- AND ClO^-

(In all experiments, ClO^- and NO_2^- mixed at pH indicated added to acid buffer. In 1.03 to 1.06, the enriched oxygen was contained in the water of acid buffer, in 1.07 and 1.08, in the ClO^- , in 1.01 and 1.02 in the water of the original solution.)

No.	(NO_2^-)	(ClO^-)	pH	E			% Transfer from ClO^-	
				NO_2^-	ClO^-	H_2O (after mixing)		
1.01	0.05	0.2	11	1.0	1.0	3.1	1.43	38
1.02	.05	.02	11	1.0	1.0	5.5	1.61	41
1.03	.2	.4	12	1.0	1.0	3.5	1.20	75
1.04	.05	.1	12	1.0	1.0	5.5	1.11	93
1.05	.05	.1	12	1.0	1.0	5.0	1.95	29
1.06	.1	.2	8	1.0	1.0	6.2	1.41	77
1.07	.1	.4	13	1.0	6.0	1.03	2.21	73
1.08	.1	.2	13	1.0	7.0	1.10	2.59	79

the majority of experiments, (Cl^-) was 1.00×10^{-2} or $2.00 \times 10^{-2} M$, but in the experiment represented by the filled-in symbol, it was $0.100 M$, and in the experiment at highest pH it was $2.00 \times 10^{-4} M$. Only a limited variation in $(Cl(I))$ was undertaken, from 0.20 to 0.68 M , and the specific rates are not affected by this change. Within the precision of the data, there is no variation of specific rate with the extent of exchange. The test of this factor was of the same quality for the present series of experiments as for those reported in Table II.

The results on the exchange of BrO^- and water are less complete than for ClO^- . In Fig. 3, the re-

TABLE II
THE RATE OF EXCHANGE OF ClO⁻ AND WATER
(Phosphate buffer at 0.1 M)

No.	pH	(Cl(I))	t	$\frac{E - E_{\infty}}{E - E_i}$	k	$\frac{k}{(H^+)} \times 10^{-8}$
2.01	9.55	0.20	15	7.6	0.13	4.6
2.02	9.75	1.02	10	3.5	.12	6.8
2.03	9.75	1.02	20	4.6	.077	4.3
2.04	9.75	1.02	30	8.5	.071	4.0
2.05	9.85	0.68	10	2.1	.076	5.4
2.06	9.85	.68	20	3.4	.061	4.4
2.07	9.85	.25	10	2.3	.082	5.9
2.08	9.90	.34	15	2.8	.067	5.4
2.09	9.90	.34	30	4.2	.047	3.7
2.10	9.90	.34	45	15.7	.061	4.8

sults obtained for the direct exchange of BrO⁻ and water are shown, as well as those for the reaction catalyzed by Cl⁻ and by Br⁻. To some extent, the data for the direct reaction and that catalyzed by Cl⁻ constitute a test of the order with respect to (Br(I)). The variation of (X⁻), 1×10^{-2} to 2×10^{-2} was too slight, and the data were too imprecise for the results to be taken as demonstrating the order of the reaction with respect to (X⁻).

Discussion

The data on the exchange of hypochlorite and water establish the kinetic law for the principal path under the conditions of our experiments to have the form $k[(ClO^-)/(OH^-)]$ and for the Cl⁻-catalyzed path to have the form $k[(ClO^-)(Cl^-)/(OH^-)]$. The rate laws for the exchange of hypobromite with water have not been tested in all their features as thoroughly as those for hypochlorite, and in adopting the forms shown in Table III, to a large extent analogy with the hypochlorite system has been relied on. The highest rates have been chosen to fix the values of the coefficients.

The quantitative conclusions from the work are summarized in Table III.

Assuming the analysis of errors to be correct, the coefficients in the empirical rate laws A, B, C and D are believed to be accurate within 30% and that for rate law E, to within a factor of 2. The coefficients in the derived rate laws depend also on the equilibrium quotients for the hypochlorite hydrolysis reactions. The values of these quotients as calculated from the dissociation constants of the acids and of water at zero ionic strength have been used. For the dissociation constant of HOCl,² 3.4×10^{-8} has been selected and for that of HOBr,³ 2.4×10^{-9} . The assumption made in calculating the concentrations of OH⁻ and the concentration hydrolysis quotient may have introduced additional error, perhaps by as much as a factor of 1.5, into the coefficient of the derived forms of the rate laws but leaving their ratios almost unaltered.

Although the rate law terms of Table III represent the principal exchange paths for the ranges of concentration covered in our work, other paths must be considered and the data have been used to calculate upper limits for the specific rates by rival

(2) As calculated by R. E. Connick, *THIS JOURNAL*, **69**, 1509 (1947), from data at lower temperatures.

(3) Measured as 2.0×10^{-9} at 20° and low ionic strength (L. Farkas and M. Lewin, *ibid.*, **72**, 5766 (1950)) and as 2.1×10^{-9} at 22° (E. A. Shilov, *Zhur. Fiz. Khim.*, **24**, 702 (1950); *C.A.*, **44**, 10445 (1950)).

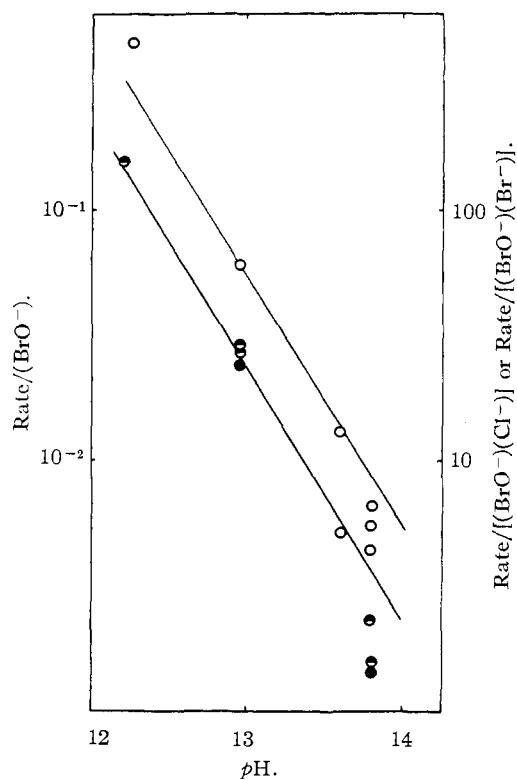


Fig. 3.—Specific rates for the exchange of BrO⁻ and H₂O as a function of pH: O, uncatalyzed, ordinate scale on left; ●, catalyzed by Cl⁻, ordinate scale on right; ●, catalyzed by Br⁻, ordinate scale on right.

paths. The conclusions concerning some other important and simple paths are summarized in Table IV.

The upper limit for the coefficient of rate law I' was calculated assuming that at pH 8.7, at which acidity the rate of exchange is fairly well documented, exchange by path F does not exceed that given by the theoretical line in Fig. 1; for rate law G, by making a similar assumption at the highest pH of measurement, 12.4; for H and K assuming that the rates by these paths in the experiments at (ClI) = 1 M and pH 9.75 do not exceed the rates actually measured.

The only reasonable mechanism for exchange by paths B, D and E is attack by X⁻ on the halogen part of HOY. Substitution by X⁻ on oxygen does not lead to the exchange measured (although it does lead to halide exchange) and exchange by an electron transfer process in which HO⁻, X and Y are formed is not energetically possible. A straightforward interpretation of the present data would appear to be: HOY + X⁻ = HO⁻ + YX. This interpretation⁴ is, however, ruled out by the observation that when X = Y = Cl, exchange of chlorine between Cl⁻ and ClO⁻ can actually be slower than that observed for H₂O-ClO⁻ as catalyzed by Cl⁻.⁵ Thus, whatever the nature of the

(4) This obvious interpretation was given to the results by H. Taube, *Rec. Chem. Progress*, **17**, 25 (1956), but in the light of the results of the experiments on Cl⁻-ClO⁻ in exchange, must be rejected.

(5) This observation was first made by R. A. Silverman in these laboratories. Complete results on the Cl⁻-ClO⁻ exchange have been obtained by (5a) M. Anbar, S. Gutmann and R. Rein and will soon be published.

TABLE III
 SPECIFIC RATES FOR THE PRINCIPAL EXCHANGE PATH

	Empirical law	Rate coefficient ^a k	Derived law	Rate coefficient k'
A	$k_A \frac{(\text{ClO}^-)}{(\text{OH}^-)}$	3.5×10^{-6}	$k_A'(\text{HOCl})$	12
B	$k_B \frac{(\text{ClO}^-)(\text{Cl}^-)}{(\text{OH}^-)}$	3.0×10^{-3}	$k_B'(\text{HOCl})(\text{Cl}^-)$	1.0×10^4
C	$k_C \frac{(\text{BrO}^-)}{(\text{OH}^-)}$	5.6×10^{-3}	$k_C'(\text{HOBr})$	1.3×10^3
D	$k_D \frac{(\text{BrO}^-)(\text{Cl}^-)}{(\text{OH}^-)}$	2.3	$k_D'(\text{HOBr})(\text{Cl}^-)$	5×10^5
E	$k_E \frac{(\text{BrO}^-)(\text{Br}^-)}{(\text{OH}^-)}$	2	$k_E'(\text{HOBr})(\text{Br}^-)$	2×10^5

^a Conc'n. of OH⁻ calculated as antilog (pH - 14).

 TABLE IV
 SPECIFIC RATE LIMITS

Path	Term	Upper limit for coeffic.
F	$k_F(\text{H}^+)(\text{HOCl})$	5×10^9
G	$k_G(\text{OH}^-)(\text{HOCl})$	400
H	$k_H(\text{ClO}^-)(\text{HOCl})$	25
J	$k_J(\text{HOCl})(\text{HOCl})$	5×10^3

attack of Cl⁻ on Cl of HOCl, the atoms of chlorine do not become equivalent. A possible interpretation is that an intermediate [HOClCl]⁻,⁶ analogous to Br₃⁻ for example, is formed, in which the terminal groups are very labile to exchange, this exchange being of the S_N2 type.

From the value for the coefficient of the kinetic term (HOCl)(Cl⁻) and the equilibrium constant⁷ of the reaction Cl₂ + OH⁻ = HOCl + Cl⁻, an upper limit of 4.7×10^{14} can be calculated for the specific rate of the reaction of OH⁻ with Cl₂. This value happens to coincide with that calculated by Morris⁸ from early measurements⁹ of the rate of hydrolysis of Cl₂. The agreement is accidental; the experimental basis for Morris' conclusions was entirely removed by later work,¹⁰ in which no decline in the first-order specific rates for the chlorine hydrolysis, as HCl increases, was observed. The rate determining step in the hydrolysis of chlorine under the conditions of the experiments by Shilov and Solodushenkov is Cl₂ + H₂O and not Cl₂ + OH⁻. The conclusions and results of these authors have been checked by measurements of the rate of the reverse reaction.^{5a}

It seems likely that exchange by paths A and C is of the type S_N2. Comparison of the exchange rate with those shown by oxygen bases known to attack HOCl by S_N2 mechanisms suggest this conclusion. It finds the strongest support in a comparison of the specific rate measured, 12 min.⁻¹, with that measured for the kinetically similar term in the reaction of HOCl with phenol and certain other substances,¹¹ the coefficient for which is 0.75×10^{-2} min.⁻¹. If

(6) J. O. Edwards, *Chem. Reviews*, **50**, 455 (1952).

(7) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 59.

(8) J. C. Morris, *This Journal*, **68**, 1092 (1946).

(9) E. Shilov and S. Solodushenkov, *Acta Physicochem. (U.S.S.R.)*, **20**, 667 (1945).

(10) E. Shilov and S. N. Solodushenkov, *J. Phys. Chem. (U.S.S.R.)*, **21**, 1159 (1947).

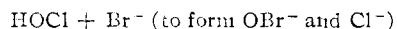
(11) P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, *J. Chem. Soc.*, 1290 (1954).

the latter measures the rate of the S_N1 path corresponding to the formation of HO⁻ + Cl⁺ or some other intermediate, it is evident that the exchange of HOCl with water does not wait on the formation of this intermediate.

If the specific rate observed for the exchange of HOCl with water is referred to the binolecular process HOCl + H₂O, the rate coefficient becomes 0.22. This value can be compared to those reported by Anbar and Dostrovsky¹² for the reactions, as 2nd order processes, of HOCl with HOCl, HOAc and H₃PO₄: 24, 5.7 and 8.2, respectively. Another comparison from the paper of Anbar and Dostrovsky which has application to the present work is that of the rate coefficient for the reaction of HOCl with HOAc as 5.7, with the coefficient for the reaction of HOCl with OAc⁻ as 3.1×10^{-5} . The comparison suggests that HOAc makes use of the proton in substitution on HOCl by transferring it to oxygen of HOCl. By analogy, a similar interpretation can be advanced for the reaction of HOCl with H₂O.

The upper limit set in the present work for the rate of interaction of HOCl + HOCl is well above the various values reported, and does not help to make a choice between them. No significance can be attached to the difference between the value reported by Anbar and Dostrovsky for the rate of interaction of ClO⁻ and HOCl and the upper limit set by the present work. The value reported in reference 12 was obtained from an analysis of complex data and may reflect errors accumulated in evaluating the contributions by other paths.

An important comparison, which serves to introduce a discussion of the oxidation-reduction reactions of the hypohalites, is that of the specific rates of halide substitution in HOX measured in the present work with that reported¹³ for the reaction



Two mechanisms must be considered for this reaction. In one, Br⁻ attacks OH so that oxygen transfer occurs, while in the other, attack is on Cl, the products being formed by subsequent hydrolysis of BrCl. The data of Table III show that in acting on Br in HOBr, Cl⁻ and Br⁻ do so at about equal rates. However, the specific rate (1.77×10^5) for

(12) M. Anbar and I. Dostrovsky, *ibid.*, 1094 (1954).

(13) L. Farkas, M. Lewin and R. Block, *This Journal*, **71**, 1988 (1949).

Br^- reacting with HOCl is almost 20 times that for Cl^- substituting on Cl in HOCl . The relatively higher rate for Br^- reacting with HOCl suggests a different site of attack for Br^- , which therefore must be on oxygen.

This conclusion, by no means certain for the present system, is important to the problem of the role which H^+ may play in reactions of oxy-ions. The only reasonable place for the proton in the activated complex of composition $(\text{HOClBr})^-$ is on oxygen. If then Br^- attacks O rather than Cl in HOCl , the role of H^+ in stabilizing O for transfer is demonstrated. Definite evidence for this conclusion is found in work with the Br^- - HOBr system. The exchange of Br between Br^- and HOBr^{14} is found to be more rapid than the Br^- -catalyzed oxygen exchange of HOBr , thus demonstrating directly that Br^- attacks oxygen in HOBr . The particular function of protons in the activated complex for reactions of anions which has been described is suggested also by observations on other systems. Thus, pernitrite persists in alkaline solution but in acid is transformed rapidly to NO_3^- .¹⁵ A reasonable formulation for the activated complex in question is



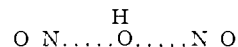
The activated complex providing for rapid exchange¹⁶ of NO with NO_2^- involves H^+ . Here

(14) M. Anbar and R. Rein, to be published.

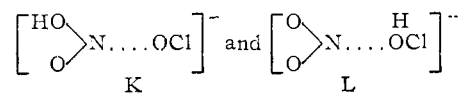
(15) K. Gleu and R. Hubold, *Z. anorg. Chem.*, **223**, 305 (1935).

(16) M. Anbar and H. Taube, to be published.

also, the location of the proton on a bridge oxygen seems the most reasonable possibility



Attempts were made in the course of the present work to decide between the activated complexes



for the reaction of NO_2^- with hypochlorite by studying the rates of reaction of $\text{RONO} + \text{OCl}^-$ and NO_2^- with ROCl . Using an aliphatic group for R , the reaction of nitrite ester is found to be very slow. On the other hand, the reaction of the hypochlorite ester with NO_2^- is very rapid, but only a small fraction proceeds to the product RONO_2 expected for formulation L . This being so, the experiment must be regarded as inconclusive on the point under consideration (a small amount of RONO_2 may appear as a side reaction of the principal change occurring), although it is consistent with formulation L for the activated complex.

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CHICAGO 37, ILL.

[CONTRIBUTION FROM THE ENRICO FERMI INSTITUTE FOR NUCLEAR STUDIES AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

The Measurement of Very Slow Reaction Rates; Decarboxylation of Alanine^{1a}

BY DWIGHT CONWAY^{1b} AND W. F. LIBBY^{1c}

RECEIVED FEBRUARY 28, 1957

A method of measuring slow reactions using radioactive labelling and low level counting techniques has been applied to the decarboxylation of alanine at temperatures corresponding to half-lives from 0.1 to 10^4 years, the results being essentially in agreement with those which Abelson obtained at higher temperatures. The half-life for decarboxylation at room temperature is found to be about 10 billion years. A side reaction, which is most probably a short chain length radiation induced reaction, was controlling below 373°K. and showed a half-life of about 10^9 years at room temperature at our specific radioactivities of about 3 millicuries of C^{14} per mole of alanine. It also was found that O_2 attacks alanine to release carboxyl carbon at a rate corresponding to a half-life of about 20000 years at room temperature.

Introduction

A Few Possible Applications of the Method.—By the use of radioisotopes the rate of very slow reactions can be measured.² Many reactions which proceed by very complicated mechanisms at high temperatures should take place by much simpler mechanisms at low temperatures since in competing branch reactions the high activation energy process will be "frozen out," e.g., the reaction of H with O_2 gives all HO_2 and no HO plus O at low temperatures. There would be no reactions of product

with product molecules because of the very low concentration of products. Also in some cases the increased stability of the products at low temperatures would simplify the mechanism. A knowledge of the low temperature mechanism should provide information (activation energies and steric factors) which would aid in understanding the high temperature mechanism.

Therefore, the application of the method to the study of many reactions should prove fruitful. Many practical applications to such problems as food spoilage probably can be made by study of especially cultured radioactive natural products.³

The method constitutes a powerful tool for the study of very slow reactions. In addition to the

(1) (a) This research was supported in part by the Office of Scientific Research of the Air Research and Development Command, U. S. Air Force Contract No. AF 18(600)-663; (b) now at Chemistry Department, Purdue University, Lafayette, Indiana; (c) presently a Member of the U. S. Atomic Energy Commission.

(2) W. H. Johnston and P. J. Manno, *THIS JOURNAL*, **79**, 807 (1957).

(3) N. J. Scully, W. Chorney, G. Kostal, R. Watanabe, J. Skok and J. W. Glattfeld, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy in Geneva," Vol. X11, 1955, p. 377.