TABLE III

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

Distance for	Model								Final results with limits of acceptability		
	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_3-Br 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.

---

[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).

LAFAYETTE, INDIANA

[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

RECEIVED DECEMBER 11, 1953

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

---

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

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

by hydrogen peroxide, the presence of a powerful $1e^-$ oxidizing agent has been demonstrated.[2] However, kinetic differences in the system are produced by substituting the acids $HClO_4$, HNO_3, H_2SO_4 for each other, which show that at least two of the corresponding anions exert specific effects. Hence the question arises in each case, whether any hydroxyl radical formed may not react with the acid anion, so that the oxidizing intermediate studied is in part at least a species derived from the anion.

A reaction which offers some hope of distinguishing between HO and other radicals is the exchange of the oxygen of the radical with water.[3] In the work reported here, we have attempted to find evidence for the participation of HO in reactions of O_3 in water solution by measuring the extent of the exchange[3] which occurs when O_3 is decomposed in water of different isotopic composition. An important difference between HO and the radicals which may be formed by it, or rival oxygen radicals which might be assumed, is the extent of the exchange which each can induce. The advantage which ozone chemistry offers for the purpose at hand over that of hydrogen peroxide, is that here the hydroxyl is converted to the product O_2 which under usual conditions does not exchange with water, while in the reaction with hydrogen peroxide it is presumably converted to water

$$HO^* + HOOH \longrightarrow H_2O^* + HO_2$$

Reference has been made in the literature to an attempt by E. Collinson and F. S. Dainton[4] to find evidence for the exchange of hydroxyl and water, examining the oxygen liberated when H_2O_2 decomposes in water of different oxygen isotopic composition. No unique conclusion can be drawn from the failure to observe exchange using this approach. A number of causes, in addition to slowness of the exchange in question might be responsible for the failure to observe isotope mixing of the oxygen derived from H_2O_2 with the solvent.

Experimental

Procedure.—Ozonized oxygen was prepared from highest purity tank oxygen by passing the dried gas through a standard type of ozonizer. The ozonizers were of Pyrex glass; on cooling in Dry Ice–acetone, they delivered 8% O_3 in the gas stream, this concentration being sufficient for our purposes. Lower concentration levels were maintained by allowing the ozonizer to operate at room temperature or by increasing the flow rate.

Three types of reaction have been studied, the spontaneous decomposition in acid solution, the induced decomposition in acid and the spontaneous decomposition in alkaline solution. In all experiments, cells were used providing about 25 ml. of gas space for 5 ml. of solution. The reaction cells were filled by passing ozonized oxygen through the solution from which only the inducing agent was omitted, until air was completely swept out. The initial concentration of ozone in the gas was determined by analyzing the contents of a dry bulb in series with the reaction vessel. The gas mixtures in contact with alkaline solution were left to proceed to complete decomposition. Those in contact with acid solution usually contained residual ozone at the time of analysis. In these experiments, two or three separate reaction bulbs were prepared, of which one was used to yield the value of the ozone concentration at the time of analysis, and the remaining one or two were used for mass spectrometric determination of the isotope ratio of the gas. During reaction the cells were stored in the dark at 23 ± 1°, and were subjected to a gently rocking motion for stirring.

The ozone was analyzed by passing the gas carried by a stream of air through neutral potassium iodide solution, and determining the liberated iodine with standard thiosulfate. In all experiments the solution was enriched in O^{18}, and the gas was of normal isotopic composition. The isotopic composition of the solutions was estimated, knowing that of the enriched water, and taking account of the exchangeable oxygen added. The isotopic composition of the ozonized oxygen was determined by drying the gas, decomposing the ozone by heat, and analyzing the oxygen in a mass spectrometer. Any samples showing abnormally high N_2 peaks were rejected. It should be noted that no errors are introduced due to fractionation, except for the experiments in which an inducing agent is present. In these, a small fraction of the ozone oxygen is converted to water. However, even here, the effects due to fractionation can be only a small fraction of those observed due to exchange, and will affect the overall isotope ratio only in the 5th significant figure. The initial isotopic composition of the ozonized oxygen was determined by passing the gas through water of normal isotopic composition, and making the determination on the washed gas. Gas so treated invariably yielded a slightly lower value for the ratio O^{18}/O^{16} than dry gas. The reason for the difference is not known, but may be caused by a spurious component of mass 34 which is removed by the ozonization and washing. Mass spectrometer analyses requiring high precision, as in experiments with gas containing the lowest concentrations of ozone, were made on an instrument made available through the courtesy of Prof. H. C. Urey, giving a precision of 2 parts in 10^4 in the isotope ratio.

Reagents were A.R. grade. The enriched water used as reaction medium was purified by distillation from alkaline permanganate, and redistillation, using all-glass stills. Other work[2] has shown the sensitivity of the rate of decomposition of ozone to the presence of impurities even at low concentration. This factor, more than the analyses, limits the precision of the data we have obtained. Particularly when as in the experiments in acid, extent of decomposition and mass spectrometer analyses are performed on separate samples, on occasion a wildly aberrant result was obtained, attributable to an accidental impurity in one of the samples. Most of the conclusions are based on experiments for which the results have been confirmed, or for an array of data which show a systematic relation to the variation of some parameter. Apparently the grease used for the stopcocks (Halocarbon product) is without effect; no difference in behavior was noted between experiments in which the solution was in direct contact with greased seals, or those conducted by isolating the seal at the end of a tube opening to the gas phase. Ordinary stopcock greases gave very erratic results, and experiments in tubes lubricated with them showed much smaller values of the extent of exchange. The reaction vessels were cleaned with concentrated nitric acid after removing the grease with solvent, rinsed thoroughly, finally with redistilled water, and dried in an oven at 110°.

The data were treated, taking account of the change in isotopic composition of the total gas, the enrichment of the water and the amount of ozone decomposed, by calculating the fraction (X) of ozone decomposed which exchanged with the solvent to produce the observed enrichment. For induced reactions, two changes take place: net decomposition of ozone and the stoichiometric reaction of O_3 with the inducing agent. Only the ozone undergoing net decomposition was used in calculating X. The theoretical justification is that HO which reacts with the inducing agent forms water and thus does not contribute to the exchange; the empirical justification is that only on this basis are the results concordant and meaningful.

Results

Table I shows the results of the experiments in acid solution, both induced and spontaneous, Table II, for the decomposition in alkaline solution.

Discussion

In the absence of decomposition (compare results of experiments 1.11, 1.12, 1.21 and 1.22 with others)

---

[3] O. L. Forchheimer and H. Taube, THIS JOURNAL, **74**, 3705 (1953).

[4] F. S. Dainton, *Ann. Reports*, **45**, 37 (1948).

TABLE I

THE EXCHANGE OF O_3 ON DECOMPOSITION IN ACID SOLUTION

(Temp., 23 ± 1°; total pressure of gases, 760 mm., except in 1.33–1.35, N_t/N_0 represents the change in the ratio O^{18}/O^{16} on decomposition; solution 7.0- to 7.3-fold enriched in O^{18}.)

No.	Time, hr.	Inducing agents[e] and catalysts	Medium	p_{O_3}, mm.	Δp_{O_3}	N_t/N_0	X
1.11	67	3.3×10^{-3} *M* Cl^-	0.04 *M* $HClO_4$	38	7.0	1.000	....
1.12	108	3.3×10^{-3} *M* Cl^-	.04 *M* $HClO_4$	36	10.5	1.002	....
1.13	80	....	.04 *M* $HClO_4$	37	21.2	1.029_5	0.12[a]
1.14	88	....	.04 *M* $HClO_4$	36	24.5	1.027	.09[a]
1.21	17	3.3×10^{-3} *M* Cl^- 1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	33	8.5	1.000[b]	....
1.22	$7^1/_2$	1×10^{-3} *M* HOAc 1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	33	9.9	1.002[b]	....
1.31	16	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	8.4	6.4	1.045[b] 1.0045[b]	.15 .15
1.32	22	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	8.4	6.6	1.0070[b]	.21
1.33	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	8.4	4.9	1.012	.16[c]
1.34	18	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	13	8.6	1.027	.13[c]
1.35	18	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	13	6.4	1.017	.14[c]
1.36	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	17	11.6	1.013	.17
1.37	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	33	21.3	1.024	.13
1.38	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	36	21.3	1.031	.15
1.39	16	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	52	41.5	1.042	.10
1.40	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	58	47.6	1.040 1.045	.090[d] .096[d]
1.51	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	32	25.0	1.034 1.033	.13 .13
1.52	17	1×10^{-3} *M* H_2O_2	.17 *M* $HClO_4$	25	13.6	1.021	.18
1.53	18	1×10^{-3} *M* H_2O_2	.35 *M* $HClO_4$	34	9.8	1.011 1.007_0	.22 .14
1.54	17	1×10^{-3} *M* H_2O_2	.035 *M* HNO_3	28	20.5	1.017 1.021	.09 .11
1.55	18	1×10^{-3} *M* H_2O_2	.35 *M* HNO_3	28	6.5	1.000+	<.01
1.56	18	1×10^{-3} *M* H_2O_2	.02 *M* H_2SO_4	33	20.5	1.020 1.033	.11 .18
1.61	8	1×10^{-4} *M* HCOOH	.04 *M* $HClO_4$	43	10.0	1.000	<.01
1.62	9	1×10^{-3} *M* HCOOH	.04 *M* $HClO_4$	37	11.4	1.007	.08

[a] Calculated by subtracting from the decomposition the residual decomposition observed over the same time interval in the chloride inhibited reaction. This residual decomposition does not produce exchange, and presumably involves a different, possibly heterogeneous path. [b] Analysis made using the precise mass spectrometer. [c] Total pressure $^1/_4$ usual. [d] Contact with grease only in gas phase. [e] Complete consumption H_2O_2 and HCOOH.

the exchange of O_3 with water in acid solution is very slight. The exchange observed is therefore coupled to the decomposition, presumably by some intermediate which is a catalyst for the decomposition. The most definite evidence about the nature of the intermediate responsible comes from the measurement of the limiting extent of exchange at low ozone concentration. Owing to the imprecision of the data, an exact value for the limiting exchange has not been established, but the data show that of chemically reasonable values as simple fractions, a limit of $^1/_6$ fits the data best. This is the value expected with HO as the intermediate responsible. The following reaction scheme, which incorporates reactions previously discussed for the catalysis by HO of the decomposition of O_3[2,5] and a step for the exchange of HO and H_2O, is consistent with the exchange data.

$$HO + H_2O^* \longrightarrow HO^* + H_2O \quad (1)$$

$$HO^* + O_3 \longrightarrow HOO^* + O_2 \quad (2)$$

$$HOO^* + O_3 \longrightarrow HO + OO^* + O_2 \quad (3)$$

$$\text{Net: } H_2O^* + 2O_3 \longrightarrow 2O_2 + OO^* + H_2O.$$

In this scheme, reaction 3 is visualized as H atom or electron transfer (HO_2 is apparently a fairly strong acid)[6] rather than an oxygen atom transfer process. In view of the strength of the O–O bond in HO_2, such a mechanism seems more likely than O atom transfer to O_3. Since the extent of exchange in acid is independent of O_2 pressure (*cf.* experiments 1.33–1.35 and expts. 1.31–1.32) the effect is not caused by an intermediate catalyzing the exchange of O_2 and water; similarly the dependence on O_3 concentration, the exchange increasing as O_3 decreases, shows that it is not caused by catalysis of O_3–H_2O exchange. Rather, the maximum extent of the exchange is a direct measure of the number of atoms of exchangeable oxygen converted to O_2, which is offered by the intermediate over the catalytic cycle. The mechanism proposed satisfies the kinetic requirements outlined. Other intermediates have been considered. With HO_2 or HO_3 assumed as the exchangeable intermediate, the limiting value of extent of exchange in each case is expected to be $^1/_3$. The mechanism with HO_3

---

(5) J. Weiss, *Trans. Faraday Soc.*, **31**, 668 (1935).

(6) H. Taube, THIS JOURNAL, **64**, 2368 (1942).

TABLE II

EXCHANGE OF OZONIZED OXYGEN AND WATER IN ALKALINE SOLUTION

Temp., 23 ± 1°; decomp. O_3 complete in all expts.; time variable, of the order of hours).

No.	NaOH, M	Special conditions	p_{O_3}, mm.	N_∞/N_0	X
2.01	0.00031	....	27.5	1.016	0.04_6
2.03	.0010	....	35.0	1.271	.71
				1.297	.77
2.03	.0050	....	32.6	1.816	2.3
				1.860	2.4
2.04	.0055	....	31.1	1.756	2.1
				1.642	1.8
2.05	.0055	$2.5 \times 10^{-3}\ M\ Cl^-$	28.1	1.627	2.1
				1.699	2.3
2.06	.0050	$8 \times 10^{-4}\ M\ H_2O_2$	31.1	1.621	1.9
				1.655	2.0
2.07	.0055	p_{O_2} reduced to $^1/_4$	6.5	1.462	1.6
				1.442	1.5
2.08	.0055	....	12.9	1.424	2.9
				1.389	2.7
2.09	.092		31.9	2.548	4.4
				2.941	5.5
2.10	.092		22.1	2.651	6.8
2.11	1.03		30.4	1.878	2.7
				2.097	3.6
2.12	9.53		34.2	1.079	0.21
				1.079	0.21
2.13	10.15		22.0	1.075	.30
				1.062	.25

can be formulated as

$$HO_3 + 2H_2O^* \longrightarrow HO^*OO^* + 2H_2O$$
$$HO^*OO^* + O_3 \longrightarrow HO^*O + O^*O + O_2$$
$$HO^*O + O_3 \longrightarrow OO^* + HO_3$$

The limiting exchange to be expected with ClO_4 as the active intermediate cannot be arrived at as definitely as for the oxygen radicals considered. The most likely value is zero. If the radical ClO_4 retains substitution properties of ClO_4^-, it would be expected to be rather inert with respect to oxygen exchange; furthermore, even if ClO_4 did exchange oxygen with solvent, the Cl–O bond would have to be severed in some step to bring this oxygen into the gas phase. Of greater force in rejecting ClO_4 as the responsible intermediate in $HClO_4$ solution, is the experimental observation that in HNO_3, $HClO_4$ and probably H_2SO_4 solution, at least at low concentration, the extent of the exchange is nearly the same. Of the reasonable intermediates, HO is the only one that explains the exchange data and in this sense the observations on exchange constitute proof of the participation of HO in the catalytic decomposition of O_3 in water.

The interpretation advanced brings many of the additional observations immediately into line with the kinetic work on chain reactions in mixtures of H_2O_2 and O_3.[2] Foremost is the effect of Cl^- and HOAc, which inhibit both the net reaction of H_2O_2 and O_3, and the decomposition of O_3 induced by it; the exchange, which also depends on the presence of HO, is also strongly inhibited. Other paths exist for the decomposition of O_3, as at high inhibitor concentration, which presumably do not involve HO as the intermediate attacking O_3.[2] These paths are observed not to produce O_2 exchange on decomposition. At high nitrate ion concentration in acid, the exchange is also wiped out, although the decomposition is not; the kinetic data[2] also indicated reaction of the oxidizing intermediate generated by $O_3 + H_2O_2$ with some (or all) of the anions ClO_4^-, NO_3^-, $SO_4^=$. The concentration of $SO_4^=$ was not increased sufficiently in the present work to make a rigorous test of the efficiency of the reaction of HO and $SO_4^=$. Formate ion, shown by kinetic evidence[7] to yield the same intermediate for the decomposition of O_3 as does H_2O_2, also induces exchange. The conditions of the kinetic experiments and those of the exchange experiments were not identical (higher temperature and lower (O_3) in the exchange work) but the indications from the exchange results are that at higher HCOOH concentration, HO is indeed the principal catalyst for the induced decomposition of O_3. Here as in the kinetic work, the remarkable result appears that the HO chain for O_3 is supplanted by some other path, presumably involving a carbon radical, at *low* (HCOOH).

The observation made in the kinetic work that the rates of the H_2O_2 induced and the spontaneous decompositions of O_3 are sensitive to the same inhibitors indicated the conclusion that the reactions proceed by a common path. This conclusion is confirmed by the exchange results which show that the extent of exchange is very nearly the same by both paths. Thus, some mechanism exists for generating HO from O_3 in water, the HO then catalyzing the decomposition of O_3. However, other paths also operate for the spontaneous decomposition, probably including heterogeneous ones, which are not sensitive to Cl^- or HOAc, and do not cause the exchange of O_3 on decomposition.

The exchange results afford some entirely new conclusions about the properties of the hydroxyl radical. The decrease in the extent of exchange as the concentration of O_3 increases makes possible an estimate of the relative specific rate of exchange, and the reaction with O_3. The average value of O_3 concentration (average computed from mean value of the log (O_3)) in expt. 1.40, is 24 mm., corresponding to a concentration in solution of $3.1 \times 10^{-4}\ M$. This concentration of O_3 suffices to reduce X from the maximum value of 0.166 to 0.09_3. The rates of exchange and of reaction with O_3 for the experiment are in the ratio 0.093/0.073, and taking account of the ozone concentration, the corresponding specific rate ratio k_1/k_2, is 4×10^{-4}. Thus quite a low concentration of O_3 suffices to wipe out the exchange effect completely. The relative specific rate of reaction of HO with H_2O_2 as compared to O_3 is 0.32 (at 0°),[2] hence a fairly low concentration of H_2O_2 also competes effectively against exchange. The data on the variation of X with concentration of $HClO_4$ indicate no effect in the range 0.004 to 0.04 M, but indicate an increase at higher acid. The increase presumably means that the competition between exchange and reaction with O_3 is more favorable to exchange at higher acid. An explanation for this behavior is that the exchange path at low acid involves HO + H_2O, but that at higher acid, the path

---

(7) H. Taube, THIS JOURNAL, 63, 2453 (1941).

$H^+ + OH + H_2O \rightarrow$ also becomes important. It is possible that the mobility of HO is greatly increased at high acid, because of the opportunity a complex of formula H_2O^+ affords for the radical to move by electron transfer in the water lattice.

The most interesting observation made in the experiments in alkaline solution is that X in these solutions can exceed unity. This means that not only the oxygen formed by the ozone decomposed, but also additional oxygen is brought into isotopic equilibrium with the solution. The means by which the exchange occurs is not known. The qualitative kinetic observations: that the extent of exchange diminishes both at high alkali and low alkali, that it increases as the pressure of oxygen increases, and that the turnover of oxygen per molecule of ozone increases as the ozone concentration decreases are compatible with a mechanism in which an intermediate formed on the decomposition of O_3 catalyzes the exchange of OH^- and O_2. A possibility is that the hydroxyl radical ion is the intermediate in question. In alkaline solution, HO, which can be expected to lose a proton in approximately the same range of acidity as H_2O_2, will be present at least in part as O^-. The exchange of hydroxyl with water (and therefore of O^-) already has been demonstrated. The exchange of O^- and oxygen may occur *via* the reaction $O^- + O_2 = O_3^-$. The ion O_3^- is known to be formed on the reaction of O_3 and solid KOH, and has been characterized in the solid state.[8] A distinct mechanism for the exchange, in which O_3 engages in a reversible reaction with OH^-, analogous for example to the reaction of SO_2 and OH^-, also fits the observations made thus far, except possibly the dependence of exchange on (O_2). A simple means of distinguishing the two modes of action would be that followed in acid solution, to study inhibition of the exchange. Experiments of this type performed thus far lead to no definite conclusion. The failure of Cl^- to inhibit the exchange does not rule out the O^- mechanism.[9] The couple $OH^- = HO + e^-$, $E^0 = -1.9$, is not sufficiently powerful to oxidize Cl^- to Cl. If HO is further stabilized by the change $HO + OH^- = H_2O + O^-$, the oxidation becomes even less favorable. If a value of 10^{-10} is assumed as the dissociation constant of HO, E^0 for the principal couple in alkaline solution: $2OH^- + H_2O + e^-$ is -1.6 volt. Neither equilibrium nor mechanism favor a rapid reaction of O^- and Cl^-. The single experiment with H_2O_2 and O_3 merely confirms an observation which can be made more directly, that H_2O_2 and O_3 react rapidly in alkaline solution. An O^- mechanism has been proposed for the γ-ray induced chain exchange of O_2 and water in alkaline solution.[10] It is likely that the intermediate causing the catalysis in this system and that studied by us is the same. But also for the radiation induced reaction, no observations are published that definitely rule out catalysis by O_3 which may be produced at low concentration, as the cause of the exchange.

Acknowledgments.—The authors wish to acknowledge the generous help of Dr. George Edwards in making the isotope analyses using the precise mass spectrometer. The research was supported by the Office of Naval Research under contract N6-Ori-02026. The funds for the purchase of the mass spectrometer used for most of the analyses were supplied by the Atomic Energy Commission under contract At(11-1)-92.

---

[8] I. A. Karzarnovskii, B. P. Nikolski and T. A. Abletsova, *Doklady Akad. Nauk. S.S.S.R.*, **64**, 69 (1949).

[9] The report (Paper 126, Division of Physical and Inorganic Chemistry, 123rd meeting, ACS, Los Angeles, March, 1953) that Cl^- does inhibit was wrong.

[10] E. J. Hart, S. Gordon and D. A. Hutchison, THIS JOURNAL, **74**, 5548 (1952).

CHICAGO, ILLINOIS

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

Evidence for a Bridged Activated Complex for Electron Transfer Reactions

BY HENRY TAUBE AND HOWARD MYERS

RECEIVED NOVEMBER 9, 1953

The reaction of Cr^{++} with a variety of ions of the type $Co(NH_3)_5X^{++}$ as oxidizing agent takes place with quantitative transfer of X to the reducing agents. For the system with $X^- = Cl^-$, it has been shown that the transfer takes place without there being any exchange with chloride ion in solution. These observations lead to the conclusion that the activated complexes for the electron transfer reactions in question have configurations in which X makes a bond simultaneously to Cr and to Co. Any group which has unpaired electrons available for interaction with Cr^{++} is found to provide a more accessible pass for electron transfer than does the proton coördination shell of $Co(NH_3)_6^{+++}$. A bridged activated complex also explains observations made on reactions of Cr(III) complexes catalyzed by Cr^{++}. Results obtained with other oxidizing agents which are substitution-inert show that although formation of a bridged activated complex does take place, *net* transfer of the bridging group from oxidizing agent to reducing agent is not an essential feature of the electron transfer process. Strong evidence is presented in support of the view that a bridged activated complex is involved also in the action of substitution-labile oxidizing agents containing Fe(III) on Cr^{++} (or in the "catalysis" of the reaction of Cr^{++} and Fe^{+++} by anions), and in the exchange of electrons between Fe^{++} and Fe(III) species.

The formulas of most aquo ions in water are not known, and therefore the problem of the mechanism of oxidation–reduction reactions involving them goes particularly deep. Furthermore, nothing is known about the changes in the coördination spheres which may accompany electron transfer, although such information is essential to the description of the electron transfer process. Information of this kind is difficult to obtain for all but a few aquo ions, the few comprising those which yield substitution-inert products on undergoing electron transfer. The reducing agent Cr^{++} qualifies for an investigation of the kind implied. The results of a study of the products formed when it is