[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Chemical Action Produced by Alpha Particles: The Combination of Deuterium and Oxygen[1]

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Introduction.—The combination of hydrogen and oxygen under the influence of alpha rays has been the subject of many investigations.[4] As a result of these studies it is known that both gases present are ionized by the alpha particles in proportion to their pressure and their specific ionization and that both hydrogen and oxygen original ions are equally effective in bringing about combination of the two gases. Water vapor which is also present as a result of the reaction is likewise ionized and one hundred per cent. efficient in promoting this reaction. It was of interest, therefore, to study the combination of deuterium and oxygen with a view to determining its relative molecular ionization by alpha particles and its effectiveness in producing chemical action.

Experimental Procedure.—The method used is that followed by previous workers.[4] Radon was collected in a spherical glass vessel of known volume. Deuterium and oxygen were then introduced and the course of the reaction was followed manometrically.

Preparation of Materials.—Oxygen was prepared electrolytically from a nearly saturated solution of barium hydroxide and dried by passing over phosphorus pentoxide and stored over mercury until ready for use.

The deuterium used in Experiments 1 and 2 reported below was obtained from the California Isotope Company, Berkeley, Calif., (density of D_2O 1.1078). The deuterium used in Experiment 3 came from the Frick Chemical Laboratory, Princeton, N. J., and was provided by Professor H. S. Taylor.

Radon was obtained from 265 mg. of radium in solution as radium chloride. The details of collection and purification have been fully described by Livingston.[5]

Results.—In Table I are recorded the experimental data of three experiments, together with certain calculated results. In the last column are given stepwise reaction velocity constants $(k\mu/\lambda)'$ the significance of which, together with method of calculation, has been fully discussed by Lind.[6] Below each of these columns is shown the weighted averages for these values together with the corresponding values for spheres of these diameters for the reaction of hydrogen and oxygen as calculated by the method developed by Lind.[6]

TABLE I

COMBINATION OF DEUTERIUM AND OXYGEN AT 25° MIXED WITH RADON

Expt. 1. Vol. = 3.013 cc. D = 1.792 cm. E_0 = 60.35 m. c. Pressure D_2 581.5 mm. O_2 357.1 mm.

Elapsed time Days	Hrs.	Min.	$e^{-\lambda t}$	Total pressure	Calculated $P\,D_2$	$P\,O_2$	$(k\mu/\lambda)'$
0	0	0	1.0000	938.6	581.5	357.1	..
0	3	15	0.9759	883.4	544.7	338.7	..
0	20	5	.8602	774.2	471.9	302.3	16.6
1	3	20	.8136	731.3	443.3	288.0	17.3
1	21	0	.7136	642.2	383.9	258.3	18.3
2	8	0	.6571	597.5	354.1	243.4	17.7
2	18	45	.6060	564.2	331.9	232.3	15.6
3	5	0	.5613	529.4	308.7	220.7	23.3
5	4	10	.3941	425.7	239.6	186.1	17.2
7	4	15	.2748	364.1	198.5	165.6	16.7
					Wt. av.		17.8
					Calculated		26.2 (68%)

Expt. 2. Vol. = 2.9535 cc. D = 1.78 cm. E_0 = 77.07 m. c. Pressure D_2 450.3 mm. O_2 225.1 mm.

0	0	0	1.0000	675.4	450.3	225.1	..
0	8	30	0.9382	605.6	403.7	201.9	21.7
0	20	20	.8586	527.6	351.7	175.9	21.2
1	12	0	.7634	443.5	295.7	147.8	22.1
2	0	30	.6950	387.1	258.1	129.0	23.8
3	11	45	.5335	273.3	182.2	91.1	25.2
					Wt. av.		22.8
					Calculated		26.6 (86%)

Expt. 3. Vol. = 2.6046 cc. D = 1.7071 cm. E_0 = 134.28 m. c. Pressure D_2 538.0 mm. O_2 287.0 mm.

0	0	0	1.000	825.0	538.0	287.0	..
0	12	25	0.9107	637.8	413.2	224.6	16.57
1	0	0	.8352	518.2	331.4	184.7	18.89
1	14	30	.7492	385.2	244.8	140.4	22.74
3	1	0	.5784	216.3	132.2	84.1	21.14
					Wt. av.		20.15
					Calculated		28.85 (70%)

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(4) Lind, "Chemical Effects of Alpha Particles," A. C. S. Monograph, Chemical Catalog Co., New York, pp. 75, 119, 124.

(5) Livingston, *Rev. Sci. Inst.*, **4**, 15 (1933).

(6) Lind, THIS JOURNAL, **41**, 537 (1919); *J. Phys. Chem.*, **16**, 592 (1912).

Discussion of Results.—Experiments 1 and 3 agree closely and indicate that the radiochemical combination of deuterium and oxygen is approximately 30% slower than that of hydrogen and oxygen at 25° (Experiment 2 is not in good agreement, though it does differ from the hydrogen reaction in the same direction). The deuterium used in this experiment had been on hand for two and one-half months, during which time it was in contact with stopcock grease. Exchange reactions may have reduced the purity to a considerable extent. It should be borne in mind that in the calculation of reaction velocity constants as given in the foregoing table the specific ionization of hydrogen, *viz.*, 0.24 (based on 1.00 for air) was used for the specific ionization of deuterium. This appears to be justified in view of the fact that the rates of radiochemical polymerization of acetylene and of deuteroacetylene are identical within the limits of experimental error.[7] Further proof that the specific ionization of deuterium used in these calculations is the correct value is afforded particularly by Experiment 1 in the above table. In this experiment the initial ratio of deuterium to oxygen was 1.63:1. As the reaction proceeds the divergence from the stoichiometric ratio rapidly increases. Thus at the end of the experiment the calculated ratio of deuterium to oxygen is 1.2 to 1. If an incorrect specific ionization value had been used, the stepwise reaction velocity "constants" would have departed considerably from constancy. The lower reaction rate must be due, therefore, to a smaller efficiency in one or more reaction steps subsequent to primary ionization. The clustering mechanism proposed by Lind[8] is as follows

$$O_2 = O_2^+ + e;\ O_2^+ + 2H_2 = (H_2.O_2.H_2)^+ \quad (1)$$
$$O_2 + e = O_2^-;\ O_2^- + 2H_2 = (H_2.O_2.H_2)^- \quad (2)$$
$$(H_2.O_2.H_2)^+ + (H_2.O_2.H_2)^- = 4H_2O \quad (3)$$

Thus, four molecules of water would be formed from one pair of ions. This is somewhat higher than the experimental value found for this reaction at 25°. However, reaction step 3, ion-cluster neutralization, may not be one hundred per cent. efficient. If this mechanism is the correct one, this step might well have a still lower efficiency in the case of the deuterium–oxygen reaction.

It has been shown by Schiflett and Lind,[9] in an investigation of the temperature coefficient of the hydrogen–oxygen reaction under alpha radiation, that at temperatures only slightly above 25° a chain reaction begins to overlap the cluster mechanism. One of the chain making steps proposed

$$H + O_2 \longrightarrow OH + O$$

presumably might be somewhat less probable for deuterium and thus account for a lower reaction velocity and ion yield.

It is interesting in this connection to note that Hinshelwood, Williamson and Wolfenden[10] find for the homogeneous thermal reaction at 557° the initial rate with deuterium is about 60% of that with hydrogen. Their work on the upper explosion limit agrees with that of Frost and Alyea.[11] From this they conclude that the lower reaction rate of deuterium with oxygen is due to a greater relative deactivating efficiency of deuterium as compared with hydrogen, but that chain initiating steps have the same probability for the two isotopes. This is in substantial agreement with our conclusions.

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Summary

The rate of which deuterium combines with oxygen under the influence of the alpha rays of radon is found to be about 25 to 30% slower than the corresponding rate of the combination of hydrogen and oxygen.

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