ucts of oxidation of hydrazine with the exception of nitrogen itself. Qualitatively it was found that the reaction, like other auto-oxidations, is affected by substances like acetanilide, aniline, hydroquinone, etc.

Summary

1. The auto-oxidation of hydrazine in alkaline solution has been studied by the procedure of passing oxygen through a fritted glass disk into the solution.

2. With this procedure the reaction is heterogeneous and the rate may be expressed by the equation $-dC/dt = k \times p_{O_2} \times C^{1/n}$, being governed by the rate of adsorption of hydrazine on the active surface.

3. Hydrogen peroxide is formed under all conditions when hydrazine in dilute alkaline solution is exposed to the action of oxygen.

4. The rate of oxidation passes through a maximum, in the presence of sodium hydroxide, with increasing concentration of hydroxide. The optimum concentration corresponds with that for the maximum rate of decomposition of hydrogen peroxide by colloidal materials, indicating that the auto-oxidation is also a micro-heterogeneous reaction.

CORVALLIS, OREGON

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

OZONIZATION AND INTERACTION OF OXYGEN WITH NITROGEN UNDER ALPHA RADIATION

BY S. C. LIND[1] AND D. C. BARDWELL[2]

RECEIVED MAY 22, 1929 PUBLISHED SEPTEMBER 5, 1929

The following experiments were made about three years ago as a part of our general study of chemical reactions produced by alpha rays. Detailed publication[3] was delayed in the hope that the work could be made more complete in certain respects. Recent results of others for the same reactions, but using high-speed cathode rays, which will be fully discussed later, indicate that maximum yields per ion pair can be approached only with such high rates of gas flow and with such low intensity of discharge that it appears uninviting to attempt with alpha radiation to push farther in either of these directions than has already been done. The results given here for the formation of oxides of nitrogen, although rather incomplete, represent the first ionic yields to be reported for this important reaction.

Ozonization.—The production of ozone is studied both in pure oxygen and in mixtures with nitrogen. This was begun as a continuation

---

[1] Director of the School of Chemistry, University of Minnesota.

[2] Research Chemist, Atmospheric Nitrogen Corporation, Syracuse, New York.

[3] Brief mention was made of the results in "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., New York, **1928**, 2d ed., pp. 83 and 92.

of the earlier work of Lind[4] whose results showed considerable fluctuation in yield, believed to have been due to accidental small amounts of mercury in the ozonizing chamber, which caused high and variable de-ozonization.

More recently D'Olieslager[5] has reported new results in ozonization by alpha rays. In a static system of oxygen mixed with radon he found little or no ozone, but upon adopting the original method of Lind[4] of flowing oxygen past an alpha ray bulb and measuring ozone chemically in the effluent gas, he was able to obtain a yield of ozone of 1 molecule per ion pair, or twice the maximum obtained by Lind. He furthermore made the important observation that the yield is a function of the flow and of the intensity of radiation so that owing to de-ozonization by the alpha rays the net yield per ion pair is highest for the lowest concentration of ozone.

Experimental

The present experiments were made also using the original method except for elaborate precautions against the presence of mercury in the ozonizing chamber or flow system. While the new results (Table II and Fig. 1) are not without some fluctuation, they show great improvement over the original ones. They confirm D'Olieslager's claim of dependence of yield on ozone concentration, and under the best conditions show yields considerably higher than his. This point will be discussed further.

D'Olieslager[5] first suggested a method of calibrating the alpha-ray bulb system for ionization by means of a reaction of known M/N ratio. The failure in employing acetylene polymerization ($M/N = 20$) and the later success with $2CO + O_2 = 2CO_2$ ($M/N = 6$) have been discussed elsewhere by one of us.[6] The latter method was employed for standardization in the present work. Electrolytic gas ($2H_2 + O_2 = (2H_2O)$; $-M/N = 6$) may be employed even more conveniently, but preferably at double the

TABLE I

CALIBRATION OF ALPHA-RAY BULB SYSTEM FOR IONIZATION BY THE REACTION $2CO + O_2 = 2CO_2$ (ABSORBED IN CAUSTIC)

$E_0 = 0.1975$ curies; vol. of reaction bulb, 518.3 cc.; of absorbing bulb, 27.0 cc.; of trap, 3.4 cc.; of connecting tubes, 11.0 cc.; total vol., 563.7 cc.

Date	Hour	Time		$e^{-\lambda t}$	Vol. of gas, N. T. P., cc.	Vol. change per curie. (press. const.), cc.
		days	hrs.			
Aug. 11	4:00 P.M.	0	0.0	1.00000	527.59	. . .
Aug. 11	9:30 P.M.	0	5.5	1.95959	522.28	665.4
Aug. 12	1:00 P.M.	0	21.0	1.85428	506.56	756.4
Aug. 12	11:00 P.M.	1	7.0	1.79255	496.83	795.0
Aug. 13	8:30 A.M.	1	16.5	1.73805	488.28	794.0

---

[4] S. C. Lind, *Sitzb. Akad. Wiss. Wien*, **120**, 1709 (1911); *Am. Chem. J.*, **47**, 397 (1912).

[5] J. D'Olieslager, *Bull. Acad. Roy. Belg.*, **12**, 719 (1925).

[6] Lind, ref. 3, p. 90.

pressure of the $2CO + O_2$ mixture on account of the lower stopping power of hydrogen for alpha rays. The pressure of either mixture should be so regulated that the ionization produced by an alpha particle in traversing the radius of the reaction sphere shall fall in the same range as that of the gas to be experimented with. As the first example of the employment of this method of calibration, a set of data is given in Table I.

Taking 794.5 as the best value for the volume change per curie, the number of molecules reacting per curie is

$$7.945 \times 10^2 \times 2.705 \times 10^{19} = 21.5 \times 10^{21}$$

Taking

$$\frac{-M_{(CO+O_2)}}{N_{(CO+O_2)}} = 6 \quad \text{or} \quad \frac{+M_{CO_2}}{N_{(CO+O_2)}} = 4$$

the number of ions produced in the gas per curie would be

$$\frac{21.5 \times 10^{21}}{6} = 3.58 \times 10^{21}$$

Using Bragg's value of 1.13 of k for O_2 and 1.015 for CO, the number of ions would be $1.13 \times 3.4 \times 10^{21} = 3.85 \times 10^{21}$.

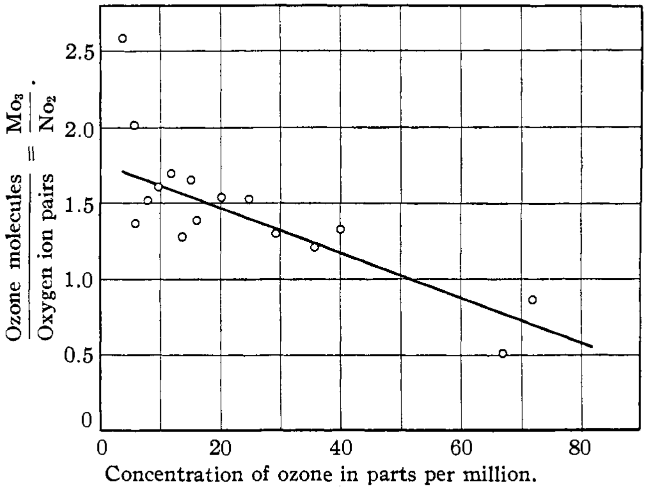

Fig. 1.

Examination of Table II and Fig. 1 will show that the M/N ratio varies from 0.5 to about 1.7 as the ozone concentration decreases from about 70 parts per million to 10 parts per million. There is one value of 2.6 for M/N and another of 2.0, but these two values are probably not consistent with the others. Values of M/N have been plotted against concentration of ozone. The values are quite irregular but there is a definite trend toward higher values of M/N as the concentration of ozone approaches zero.

Discussion of Results on Ozonization.—At present it is not possible to

TABLE II

SUMMARY OF RESULTS ON OZONE FORMATION BY IONIZATION OF OXYGEN

Date	Hour	Millicuries decayed	O_2 flow, cc./min.	O_2 flow over total interval, cc.	Ozone formed, cc.	Concn. of ozone in parts per million	$\frac{M_{O_3}}{N_{O_2}}$
6/25	4:00 P.M.						
6/25	10:15 P.M.	4.03	20	5.1×10^3	0.396	79	0.69
6/25	10:15 P.M.					72	0.86
6/26	8:30 A.M.	6.23	20	12.3×10^{13}	.860	70	.97
6/26	9:45 A.M.						
6/26	9:30 P.M.	6.5	10	7.05×10^{13}	.472	67	.51
6/26	9:45 P.M.						
6/27	2:00 P.M.	8.16	40	39.0×10^{13}	1.553	40	1.33
6/27	2:00 P.M.						
6/28	8:30 A.M.	8.16	35	39.0×10^{13}	1.39	35.6	1.21
6/28	8:30 A.M.						
6/29	8:30 A.M.	9.11	100	144×10^{13}	2.16	15	1.66
7/2	1:00 P.M.						
7/3	8:30 A.M.	3.48	160	178×10^{13}	1.00	5.6	2.02
7/3	8:45 A.M.						
7/4	11:00 A.M.	3.94	52	81.9×10^{13}	0.953	11.6	1.70
7/4	11:00 A.M.						
7/5	4:30 P.M.	3.60	25	44.3×10^3	.713	16.1	1.39
7/5	4:30 P.M.						
7/6	3:00 P.M.	2.28	15	20.2×10^3	.498	24.6	1.53
7/6	3:00 P.M.						
7/7	3:00 P.M.	2.02	150	216×10^3	.746	3.46	2.59
7/7	3:00 P.M.						
7/9	8:30 A.M.	2.78	15	37.4×10^3	.507	13.6	1.28
7/17	11:00 A.M.						
7/18	8:00 A.M.	20.8	100	132×10^3	3.87	29.3	1.30
7/18	9:00 P.M.						
7/19	8:30 A.M.	9.1	150	1000×10^3	1.99	20	1.54
7/22	8:30 A.M.						
7/23	8:30 A.M.	9.55	150	216×10^3	2.13	9.9	1.57
7/23	8:30 A.M.						
7/23	3:30 P.M.	2.53	150	63×10^3	0.578	9.2	1.61
7/23	3:30 P.M.						
7/24	8:30 A.M.	5.62	150	153×10^3	1.21	7.9	1.52
7/24	8:30 A.M.						
7/25	11:30 A.M.	7.32	150	243×10^3	1.425	5.9	1.37

predict *a priori* the yield per ion pair for a given reaction. Empirical rules have been established[7] by analogy for certain classes of reactions, but since ozonization represents a unique class, namely, a system of a single component with supposed affinity for free electrons, we have no guiding precedent. Evidently, unlike the case of components with no electron affinity, we must consider negative as well as positive ions. The negative ions

---

[7] Ref. 3, Chapter 5.

would be molecular and if we assume that the positive ions are also mainly molecular,[8] the following might represent some of the possibilities.

TABLE III

THEORETICAL O_3 YIELD

	Reactions	Per ion pair	Remarks
	No ion clustering		
1	$O_2^+ + O_2^- = O_3 + O$	>1<2	The O atom in (1) must have high velocity to carry away the heat of the ion recombination, to prevent decomposition of O_3
1a	$O + O_2 = O_3$		
1b	$O + O_3 = 2O_2$	rare	
1c	$O + O = O_2$		
	Bimolecular clusters		
2	$O_2^+\cdot O_2 + O_2^-\cdot O_2 = 2O_3 + O_2$	2	Improbable that $2O_3$ and O_2 would all remain intact
2a	$O_2^+\cdot O_2 + O_2^-\cdot O_2 = 2O_3 + 2O$	>2<4	
	Stoichiometric clusters		
3	$O_2\cdot O_2^+\cdot O_2 + O_2\cdot O_2^-\cdot O_2 = 4O_3$	<4	Improbable that all 4-O_3 molecules would remain intact

If any such reactions take place as those indicated above, yields could be expected in the range 1 to 4 molecules of O_3 per ion pair in oxygen. Although Mund and D'Olieslager[9] deduced from experiments in the presence of mercury that the maximum theoretical yield does not exceed about 1, the present results show it cannot be less than 1.5, is more probably nearer 2, while results of less certainty indicate it to be as high as 2.0 to 2.6. Undoubtedly secondary de-ozonization plays the controlling part, but it does not appear possible that it is caused by direct collision of alpha particles with O_3 molecules as has been suggested. We know the action of alpha particles is not in the least selective and therefore the chance of de-ozonization by this means at low concentration of O_3 is practically negligible. Evidently we must resort to a de-ozonizing action of activated oxygen either as ions or as atoms (see Reaction 1b).

Owing to the great difficulty of working at yet lower ozone concentration or of extrapolating, since the experimental results become progressively less accurate in that direction, it is not possible to set an upper limit to the yield, but there is no indication from alpha ray results that it would exceed 3–4 molecules of ozone per ion pair in oxygen.

Using high velocity cathode rays from a Coolidge tube, Busse and Daniels[10] have recently obtained results which confirm the ionic yields obtained with alpha rays. Since they could not measure nor calculate ionization directly, they employed the indirect method of measuring calorimetrically the energy received in their reaction chamber. Assuming it to be wholly expended in producing O_2^+ ions by electron collision, with a loss of 15 volts (the ionization potential of O_2) they obtained a yield of $M_{O_3}/N = 1$.

---

[8] H. D. Smyth, *Proc. Roy. Soc. London*, **105A**, 116 (1924).

[9] W. Mund and J. D'Olieslager, *Bull. Acad. Roy. Belg.*, Nos. 4–5 (July).

[10] Busse and Daniels, THIS JOURNAL, **51**, 3271–3286 (1929).

The earlier work of Krüger[11] with cathode rays accorded with the alpha ray results and hence with the new results of Busse and Daniels, but in later work Krüger and Utesch,[12] measuring the ionization by a supposed saturation current method, obtained much higher yields, 12 to 40 molecules of O_3 per ion pair in O_2. If, however, Krüger and Utesch were misled in believing they secured saturation current, as seems very probable on *a priori* grounds,[13] their ionization measured was too low, and hence their calculated yield too high. That this was probably the case is indicated by the fact that both Busse and Daniels and Marshall[14] have attempted to obtain saturation current under conditions similar to those of Krüger and Utesch without any indication that saturation was approached. There remains then every reason to believe that the law of equivalence of ionization and chemical action, first established for alpha rays, holds in the same way for Lenard rays. Busse and Daniels' calorimetric method of arriving at an M/N ratio is an important step in making such comparisons possible.

Interaction of Nitrogen and Oxygen. (Preliminary Experiments.)—It is rather striking that in all the gaseous reactions under alpha radiation that have been investigated, no results have been reported of the combination of oxygen and nitrogen under its influence, except a note by Soddy[15] who found that the collection of pure radon by condensation at low temperature is impossible if air is present in the gases, owing to the production of N_2O, which is also condensed at liquid-air temperature. The first compound formed in the arc process and in the oxidation of NH_3 is NO. The NO is oxidized to NO_2 (in equilibrium with N_2O_4) rather slowly in the presence of excess O_2. If NO_2 is dissolved in H_2O, HNO_2 and HNO_3 are formed in solution and some NO is liberated. This NO will oxidize to NO_2 in the presence of O_2, so that eventually all of the nitrogen is oxidized to nitrate.

Study of the combination of nitrogen and oxygen by alpha rays is greatly complicated by the simultaneous formation of ozone. A flow system was adopted like that recently used for ammonia synthesis.[16] Owing to the difficulty of determining the oxides of nitrogen and ozone separately in a flow system, the device was adopted of making alternate measurements of the total acidity by passing the gases for a time through standard alkali and then of the combined power to liberate iodine from a potassium iodide

---

[11] F. Krüger, *Physik. Z.*, **13**, 1040 (1912); "Nernst Festschrift," pp. 240–251 (1912).

[12] F. Krüger and O. Utesch, *Ann. Physik*, (4) **78**, 113–156 (1925).

[13] Lind, *Trans. Am. Electrochem. Soc.*, **53**, 26 (1928).

[14] A. L. Marshall, THIS JOURNAL, **50**, 3178 (1928).

[15] F. Soddy, "Annual Report of the Chemical Society" for 1910, Vol. 8, 299–300 (1911).

[16] Lind and Bardwell, THIS JOURNAL, **50**, 745 (1928).

solution. The oxides of nitrogen dissolving in alkali form nitrites and nitrates. The neutralizing capacity of the gas is thus a measure of the acid oxides formed and does not exceed one molecule of acid for each atom of nitrogen in the oxides. The capacity to liberate iodine is a measure of the combined oxidizing power of ozone and nitrogen oxides. All oxides of nitrogen are oxidized to N_2O_5 by ozone providing the latter is in sufficient excess. That the concentration of ozone was not always high enough to oxidize completely the nitrogen oxides to N_2O_5 in the time allowed before absorption seemed to be indicated by the results for air in which there was a marked "after-bluing" in the thiosulfate titration—in some cases amounting to 25% of the total titration. In mixtures of air and oxygen the extent of "after-bluing" became less for increasing O_2 content.

The ratio of oxygen to nitrogen was varied from that in air to about 4 O_2:1N_2 by the addition of oxygen to the stream. The total oxidizing power is found to be equivalent to 2.4 molecules of ozone per pair of ions (total) in air and decreases slightly as the mixture becomes richer in oxygen. The results are shown in Table IV.

TABLE IV

RESULTS WITH ADDED OXYGEN

Date	Hour	Flow, cc. per min. O_2	Flow, cc. per min. Air	Ratio O_2	Ratio N_2	Millicuries decayed	$\frac{M_{\text{acidity}}}{N_{\text{total}}}$	$\frac{M_{\text{ozone equiv.}}}{N_{\text{total}}}$
6/22–6/23	3:30 P.M.–8:45 A.M.	..	20	1	4	18.45	0.74	..
6/23–6/23	9:15 A.M.–2:15 P.M.	..	20	1	4	4.9	..	2.4
6/23–6/24	3:30 P.M.–8:30 A.M.	..	20	1	4	15.2	0.77	...
6/24–6/25	2:45 P.M.–8:30 A.M.	9.0	16.0	1	1	13.3	0.49	...
6/25–6/25	8:45 A.M.–1:45 P.M.	9.0	16.0	1	1	3.43	..	2.2
6/29–6/30	1:15 P.M.–9:30 P.M.	60	20	4	1	6.18	..	2.2
6/30–6/30	11:00 A.M.–9:30 P.M.	60	20	4	1	2.83	..	2.3
6/30–7/1	9:30 P.M.–9:00 A.M.	30	10	4	1	2.85	..	1.8
7/1–7/2	10:15 A.M.–8:30 A.M.	30	10	4	1	4.81	0.23	..
7/15	5:00 P.M.	Closed the reaction bulb off containing tank O_2						
7/16	12:00	Started sweeping out with O_2 at 50 cc. per min.						
7/16	2:00 P.M.					28.5	0.005	
7/19	11:00 A.M.	Closed the reaction bulb off containing air						
7/20	4:00 P.M.					19.5	0.23 cc. of N_2O	

$$\frac{M_{(N_2O)}}{N_{(\text{total})}} = 0.076$$

It is quite apparent that the formation of acidic oxides falls off as the N:O ratio in the flowing gases is diminished. Apparently this might mean that nitrogen ions, but not oxygen ions, are responsible for this reaction. If the ionization potential of nitrogen is higher than that of oxygen, then ionization by collision of the second kind[17] could take place only in the direction $N_2^+ + O_2 = N_2 + O_2^+$ which would explain at once why nitrogen oxide formation diminishes while total oxidation remains relatively little changed,

---

[17] G. P. Harnwell, *Phys. Rev.*, **29**, 683, 830 (1927).

since the latter represents both ozone and oxides of nitrogen. In the static experiment with 28.5 millicuries of radon decaying in a 4 O_2:1 N_2 mixture, very little acid was produced.

The special experiment on the production of nitrous oxide in air confirmed Soddy[15] in its formation, although the yield was only 0.076 molecules per pair of ions, much lower than that of the acid-forming oxides.

The nitrous oxide was separated from the air by use of liquid air and was subsequently pumped off at −100° into a miniature eudiometer tube. That the gas so separated was nitrous oxide was confirmed by explosion with a measured volume of pure hydrogen. The volume contraction corresponded approximately to that for the reaction $N_2O + H_2 = N_2 + H_2O$ (liq.).

Summary

1. Ozonization in oxygen flowing past an alpha-ray bulb is higher (per ion pair) the faster the rate of flow and the lower the intensity of ionization, that is, higher the lower the ozone concentration from either influence, owing to de-ozonization. This confirms D'Olieslager's results.
2. The maximum yields of ozone obtained per ion pair (M_{O_3}/N_{O_2}) was not less than 1.5 and may be as high as 2–2.5.
3. De-ozonization appears to be due to a secondary effect of oxygen ions (or atoms), not to a primary impact with an alpha particle.
4. In mixtures of nitrogen and oxygen both ozone and acid-forming oxides of nitrogen are simultaneously formed; also a smaller amount of nitrous oxide (confirming Soddy). Nitrous oxide formation was investigated only for air.
5. The yield of acid-forming oxides diminishes with decreasing N_2:O_2 ratio, while the total oxidizing power toward potassium iodide solution is little influenced. A theory is proposed for this.

MINNEAPOLIS, MINNESOTA

NOTES

An Application of the Thiocyanate Method for the Precipitation of Copper in the Confirmatory Tests for Cadmium and Antimony.—The use of the thiocyanate anion as a means for the separation of copper from cadmium, after first having reduced the copper with sulfurous acid, has been suggested by Crookes.[1] This method has also been used for the quantitative determination of copper, but to the knowledge of the author it has not hitherto been applied to the qualitative scheme of analysis. The insolubility of cuprous thiocyanate in dilute sulfuric and hydro-

---

[1] William Crookes, "Select Methods in Chemical Analysis," Longmans, Green and Company, London, 1886, p. 332.