trans molecule ever gets far out of the planar state, we may conclude that it will rapidly lose for good its electronic vibration.

Since *trans* molecules when excited by light of 2537 Å. have an internal energy of more than 20 kcal. above the state $^*T_0$, and yet nearly half of these molecules fall to the state $^*T_0$ and then fluoresce, we cannot avoid the conclusion that a high potential barrier, against rotation about the double bond, is present in the electronically excited *trans* states. This barrier, however, as far as our experiments show, may be considerably less than it is in the normal state.

Summary

The fluorescence and absorption spectra of *cis* and *trans*-stilbenes have been studied. The quantum yield in the conversion of each isomer into the other by light of 2537 Å. has been determined. These experiments permit a calculation of the upper limit to, and the probable value of, the fluorescence yield of *trans*-stilbene. The results are interpreted in terms of the "loose bolt" theory of Lewis and Calvin, and of Olson's theories regarding the electronically excited states of *cis* and *trans* isomers.

Berkeley, Calif. Received July 17, 1940

[Contribution from the Bureau of Plant Industry, U. S. Department of Agriculture]

The Oxidation of Nitrogen in an Ozonizer Discharge at High Temperatures[1]

By J. F. Shultz[1a] and Oliver R. Wulf[1b]

Introduction

Much work has been done during the last fifty years on the oxidation of nitrogen in various forms of electrical discharges, and a portion of this work has been given to the study of the oxidation in discharges of the form occurring in ozonizers. The general field has been covered recently by Glockler and Lind[2] in their book on the electrochemistry of gases. Since a comprehensive survey of this subject is available, no attempt to cover the field will be made in this paper. The object of the present research was to study the oxidation of nitrogen in the silent electrical discharge under conditions for which the existing data were either insufficient or lacking, namely, at atmospheric pressure and over a range of temperatures extending sufficiently high that, if possible, the naturally limiting thermal decomposition of nitric oxide should be reached. These conditions should favor high reaction rates in the secondary chemical reactions involved, and would tend to prevent any of these being limiting factors in the oxidation. Fischer and Hene[3] had found that the amount of oxidized nitrogen formed in air flowing at a constant rate through a quartz ozonizer became greater at higher temperatures, increasing up to 700°, the highest temperature they give.

It is notoriously difficult to measure electrically the power dissipated in an ozonizer and no attempt to do this was made in the present work. Nor was any direct attempt made to study the primary electrical process occurring in the gas. The results of this work concern the relative rates of the reactions of formation and of decomposition of oxidized nitrogen in the discharge and not the electrical efficiency, though they bear upon the latter. However, certain observations made in the course of this and related work,[4] together with the results of an oscillographic study of the ozonizer discharge described in a recent paper by Klemenc, Hintenberger, and Höfer,[5] have led the authors to some conclusions concerning the physical behavior of an ozonizer which will be included in the discussion of the results.

Experimental

The principal arrangement of apparatus employed is shown in Fig. 1. Mixtures of nitrogen and oxygen in varied proportions were passed through an ozonizer at known rates of flow, the gases coming from tanks, through flowmeters, and through drying spirals immersed in a mixture of solid carbon dioxide and alcohol. After passing through the ozonizer, the gases were mixed with a small amount of ozonized oxygen from an auxiliary water-cooled ozonizer

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[1] Not subject to copyright

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[2] Glockler and Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

[3] Fischer and Hene, *Ber.*, **45** 3652 (1912)

[4] Wulf and Melvin, *Phys. Rev.*, **55**, 687 (1939).

[5] Klemenc, Hintenberger, and Höfer, *Z. Elektrochem.*, **43**, 708 (1937).

to provide an excess of ozone in all cases, ensuring that nitric oxide and all higher oxides produced in the ozonizer were in the form of nitrogen pentoxide.[6] These gases passed through water in two efficient gas scrubbers placed in series, the oxidized nitrogen being absorbed in the first of these as nitric acid, the second indicating that no appreciable amounts of oxidized nitrogen escaped the first scrubber. Nitrogen pentoxide is very readily taken up by water.

The contents of the first scrubber, after a fixed time of operation of the ozonizer and a subsequent interval of flushing, were withdrawn and raised to boiling to destroy the excess ozone. Because of the excess ozone added from the auxiliary ozonizer, an excess was always present even at high temperatures where only the lower oxides and thus no ozone came from the main ozonizer. The sample was then cooled and titrated against standard 0.01 N sodium hydroxide solution using phenolphthalein as an indicator. The presence of ozone in the solution interfered with the use of the indicator. Times of operation of the ozonizer of eight minutes or twenty-four minutes were ordinarily employed. The longer of the two intervals was resorted to because of the relatively small amount of nitric acid collected in such runs, the solution obtained being in amount about 100 cc. and of the order of 0.001 N in nitric acid. The exit gases containing ozone were passed into a small open Bunsen flame which destroyed the ozone.

Because of the small amount of nitric acid collected in time intervals short enough to be compatible with the taking of a number of samples each day, the results of the titration were subject to an error of 0.5–1%, this varying somewhat of course with the amount of acid collected. This was, however, adequate for the present work whose aim was to study the changes in the behavior of the oxidation occurring in the ozonizer over a wide variation of conditions, rather than to study in detail the behavior under one set of conditions. By far the largest source of uncertainty throughout this work lay in the variability of the ozonizer action itself, a phenomenon having to do with the variability of the condition of the interior surfaces of the dielectrics. It was, however, found that, with care and time, a quartz ozonizer settles down to a remarkably constant behavior.

The oxygen used in the auxiliary ozonizer contained a little nitrogen as an impurity and hence a small amount of nitrogen pentoxide was produced in this ozonizer. This was determined and a constant correction was made for it.

A number of ozonizers were used during the course of this work. The first few were of Pyrex. However, to cover the temperature range desired, quartz ozonizers were necessary, and the principal results to be reported in this paper refer to ozonizers of fused quartz. They were of the double dielectric conventional type, with metal coatings on the inside of the inside cylinder and on the outside of the outside cylinder.

These metal coatings for use at high temperatures were a matter of considerable research. Thin sheet nickel was finally used, being simply pressed against the quartz surfaces. Though subject to slow oxidation at the highest temperatures, they stood up very satisfactorily.

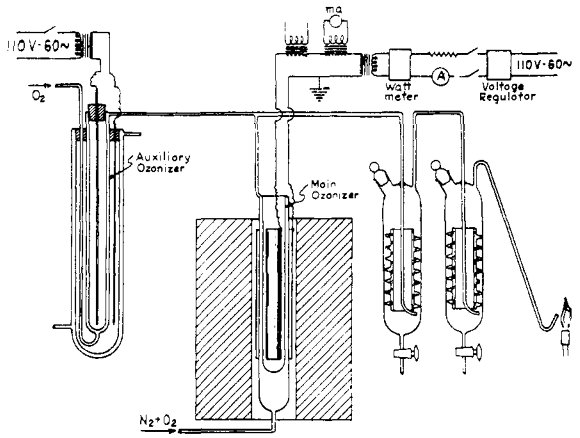

Fig. 1.

Measurements were made from room temperature to 1000°. The ozonizer was surrounded with a resistance furnace mounted on fire bricks, and the temperature was measured by means of a thermocouple placed against the outer wall of the ozonizer. The outer electrode of the ozonizer was grounded, the high voltage, 60 cycle supply coming from a Thordarson transformer, type R, 110–25,000 volts, 1000 volt-amperes, which was fed in the final work by a Sola constant voltage transformer, the 110 volt drop from this occurring in part across a fixed resistance in series with the primary of the high voltage transformer. The voltage across the primary of the latter was ordinarily about forty volts.

In the measurements leading to the final results, power and current were measured at the primary terminals of the transformer and an a. c. milliameter in the secondary circuit gave indications of changes occurring in the 60-cycle current flowing in the ozonizer circuit. The wattmeter was actually used in correcting for small fluctuations, which occurred in the electrical behavior of the ozonizer even after the ozonizer had been well conditioned and was operating in a quite stable manner. Such small variations, which are very difficult to eliminate, went hand in hand with, and were approximately proportional to, small changes in the amount of nitric acid collected. Since the transformer with secondary circuit open dissipated considerable power, the difference in wattmeter reading for the ozonizer in operation and that for open circuit was the power quantity, hereafter spoken of as the power, taken as a measure of the intensity of the ozonizer discharge for the purpose of correcting for the small variations in yield described above. The titration was divided by this nearly constant power quantity, thus correcting in an approximate manner for variations which were themselves small. These values were used to calculate the *relative* rates of the formation and the decomposition of oxidized nitrogen in the discharge, which are the principal results of this work. Naturally no significance is to be attached to these results in the sense of chemical yield per unit of electrical energy expended.

Preliminary Results

Early exploratory runs gave a general picture of the dependence of the yield of oxidized nitrogen

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(6) Concerning reactions involved see for example Busse and Daniels, THIS JOURNAL, **49**, 1257 (1927); Wulf, Daniels, and Karrer, *ibid.*, **44**, 2398 (1922).

on the temperature and upon the nitrogen–oxygen ratio. They covered the temperature range from room temperature to 1000° for air, and at 650° a number of nitrogen–oxygen ratios. They were made, however, during a period when the particular quartz ozonizer was still in the conditioning process and thus was not entirely stable or reproducible. However, the results were adequate to show the general character of the behavior which may be described as follows.

When air is passed through the apparatus at sufficiently high rates of flow, the amount of nitric acid collected for a constant time of operation of the ozonizer increases with temperature from room temperature to 800°. The rate of increase varies with temperature, however, and at low rates of flow a maximum appears in the vicinity of 100°. Above 800° the amount of nitric acid collected falls rapidly, to a value near zero at 1000°. This behavior is shown in Fig. 2.

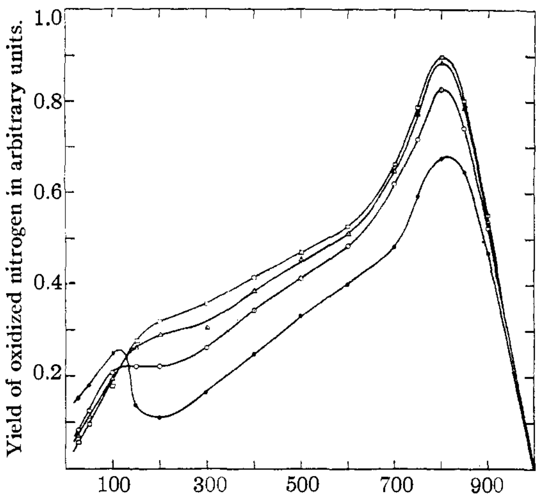

Fig. 2.—Air, cc. per min.: ●, 100; ○, 300; ◬, 500; ⊡, 700.

The amount of nitric acid collected for constant time of operation of the ozonizer discharge and at constant temperature also varies when the relative proportions of nitrogen and oxygen in the gas mixture are varied. This relation has a maximum at high nitrogen ratios. The value and the position of this maximum change with rate of gas flow, increasing and moving toward higher nitrogen ratios with increasing flow. Figure 3, showing results obtained at 650° and two rates of flow, illustrates these points. The figure is, however, a composite of data obtained for two different time intervals of running the discharge, namely, eight minutes and twenty-four minutes. Data at a number of different nitrogen–oxygen ratios using the eight-minute discharge interval gave the trend of these curves, while other data using simply air and 92% nitrogen–8% oxygen and a twenty-four-minute interval of discharge gave the four points indicating the maxima. The means of the eight-minute interval data were converted to the scale of these four points by multiplying by a conversion factor determined from the values of these four points and the corresponding points of the eight-minute interval data.

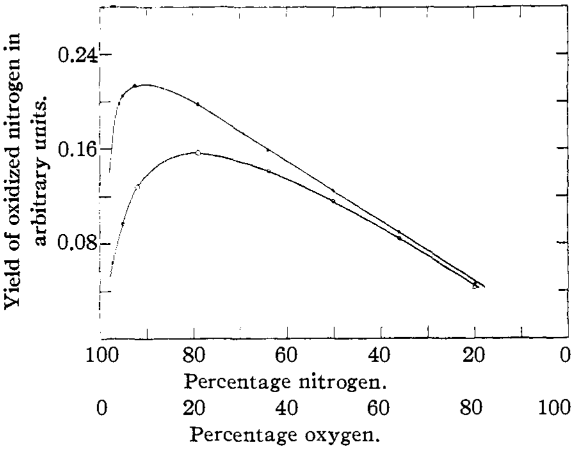

Fig. 3.—Gas, cc. per min. at 650°: ●, 500; ○, 100.

It is to be noticed that, as described earlier, the ordinates are the yields of nitric acid in arbitrary units for constant time of operation of the ozonizer without direct reference to the power taken by the ozonizer. Thus no indication is given in the data of these figures as to the extent to which the variations in the yield are caused simply by changes in the physical character of the electrical discharge in the ozonizer with temperature and composition of the gas mixture.

Figure 2 shows in detail the behavior that was indicated by the few results given by Fischer and Hene[3] and illustrates certain interesting points. For temperatures above 200° the yield, for constant time of discharge, increases with increasing flow as would be expected, though below 100° the reverse is true.[7] The fall of the yield above 800° is very abrupt.

(7) Below 100° the data of Fig. 2 show that the yield for constant discharge time increases with decreasing rate of flow. This unusual behavior, the reverse of that ordinarily to be expected, suggests that an increase in the rate of formation of oxidized nitrogen occurs with increase in the concentration of N_2O_5 and O_3 in the gas mixture, since this latter evidently increases in any case when the rate of flow is

The character of the data of Figs. 2 and 3 has been checked in the course of the work, but numerical values were not ordinarily reproducible because of change in the ozonizer with time. For instance, the data of Fig. 2 were collected over the interval of a few days. Later the same ozonizer was giving different yields, but this is characteristic of such an apparatus and, we believe, easily understood in view of the nature of the discharge, though not easily controlled.

Character of the Discharge

The discharge in an ozonizer consists of a myriad of tiny sparks, which represent the discharge across the intervening gas space of the two ion layers, accumulated on the two dielectric surfaces.[4] The number and uniformity of the tiny sparks are greater the smaller the tiny surface area which any one spark can discharge, that is, the smaller the surface conductivity of the dielectric. When dry nitrogen–oxygen mixtures are passed through an ozonizer this condition improves with time of operation. In a well-conditioned apparatus the discharge was a nearly textureless blue glow, and the chemical action of the discharge very constant. If the temperature is raised considerably above that at which the ozonizer has been conditioned, a new period of change sets in, the ozonizer ultimately becoming stable in its chemical behavior again at this temperature. It seems reasonable to suppose that this is connected with the further driving out of material adsorbed or otherwise held on the walls of the dielectric. Over a period of several days, at least, such an ozonizer will give reproducible results at temperatures up to the one at which it has been conditioned. It is believed that the walls of the dielectric are in equilibrium with the constituents of the gas mixture, as for example, with the water vapor in air dried by cooling to the temperature of solid carbon dioxide. This is very little water vapor, but surface conductivity is a sensitive thing. The introduction of a constituent[4] such as nitrogen pentoxide, which is a strong drying agent, into the gas mixture would certainly be expected to affect somewhat the partial pressure of water vapor in the gas and, thus, the amount of water vapor adsorbed in the surface of the dielectric. This in turn would alter the character of the discharge,[5] that is, the number, the frequency of occurrence, and the intensity of the many little sparks and thereby the chemical action of the ozonizer. Such a description is very much in accord with the often seemingly erratic behavior of ozonizers.

Results

Having determined the general character of the change with temperature and composition of the amount of oxidized nitrogen issuing from the ozonizer, the causes of these changes were sought by studying the rates of the reactions of formation and decomposition for air over the temperature range 250–650°, and at 650° for a series of nitrogen–oxygen ratios lying in the range 50% nitrogen–50% oxygen to 96% nitrogen–4% oxygen. To do this three points on the curve of yield against rate of gas flow were determined at 100, 300, and 500 cc./min., respectively. A large number of runs were made during the course of the work in which, each day, three such determinations were made for two different temperatures or two different gas compositions, plus one or sometimes two further determinations at the end of the day's work. These last were made under the same conditions as the first and second determinations at the beginning of that day. This provided a control of the constancy of the electrical behavior of the ozonizer over that day. Unless the first and last analyses checked well with one another, the data of that day were not used in the final results.

The three determinations at three different flows give three points on a yield *versus* rate of flow curve. This curve must pass through the origin of these coördinates. The concentration of oxidized nitrogen, hence the rate of its decomposition, is negligible for very high rates of flow. Therefore at high rates of flow the curve must become asymptotic to a value of the yield

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decreased. Such behavior, furthermore, requires that there be an optimum rate of flow, since for rates of flow approaching zero the yield must also approach zero. This was investigated at 28 and 100° and the optimum flow found to be about 125 cc./min. Another possible cause of such behavior might lie in a change in the character of the gas flow with changing rate of flow, but at higher temperatures the yield changes normally with rate of flow. It seems probable that this behavior finds its explanation in the circumstance demonstrated by Ehrlich and Russ[9] that, with increasing O_3 and N_2O_5 concentration, *an increase in breakdown* potential and an increase of the potential across the gas space occur. Such an explanation would lead one to expect that in the static runs made by these authors at room temperature a point of inflection might occur in their curves early in the time of running. While their figures do not show such, it seems possible that this may have occurred in a time interval shorter than would be shown in their figures. If, in the present work, the time spent by any portion of the gas in the discharge may be calculated from the volume of the discharge space and the rate of flow, then for flows of 100 cc./min. and greater the time spent by any portion of the gas in the discharge was one-half minute or less.

numerically equal to the pure rate of formation multiplied by the time of operation of the discharge. On the other hand, the slope with which this curve passes into the origin is essentially a measure of the limiting concentration of oxidized nitrogen reached in the ozonizer under conditions of zero flow, and is a measure of the ratio of the specific rates of formation and decomposition. Knowing the rate of formation and this ratio, the rate of decomposition is immediately determinable.

The measurements at three flows sufficed only to determine approximate values of these two rates but this was adequate to investigate the effects of temperature and nitrogen–oxygen ratio, and was compatible with the carrying out of a large number of runs that was requisite because of the changes which the discharge of the ozonizer undergoes.

This manner of obtaining the two relative rate constants may be looked upon as a graphical one, with no assumption as to the order of the reactions except that there is a constant rate of formation (for constant discharge conditions) and a rate of decomposition which increases with increase of the concentration of the material undergoing decomposition. All the data are in accord with this picture. Whether the decomposition increases with the first or another power of the oxidized nitrogen (presumably principally nitric oxide at these temperatures and partial pressures) is another matter.

It was found most convenient to treat the data by means of expressions derived by assuming a first power and a second power dependence, respectively. The experimental results indicated conformance with a power lying between the first and second, though the agreement with the first power expression seemed somewhat better than with the second. The use of either expression would lead to the same general conclusions, however, and the use of one affords a consistent method of determining the asymptote and the initial slope of the curve.

If C is the concentration of nitric oxide attained in the time t during which the flowing gas is in the discharge zone of the ozonizer, then the amount of material Q collected from a time of operation of the ozonizer τ is given by

$$Q = C\tau r \qquad (1)$$

The time t evidently is equal to v/r if v denotes the effective discharge volume of the ozonizer and r the rate of gas flow. If a decomposition depending on the first power of the NO is assumed, the concentration C is obtained by integrating the differential equation

$$+\frac{\mathrm{d}C}{\mathrm{d}t} = k - aC \qquad (2)$$

where k is the rate of formation of oxidized nitrogen and a is the specific rate of its decomposition. The rate of decomposition depends also, of course, on the concentration of oxidized nitrogen. The two constants as explained above are in arbitrary units and serve, upon comparison, to show the relative rates of formation and decomposition, the quantities sought in this research, as a function of temperature and composition of the gas mixture. This integration yields

$$C = \frac{k}{a}(1 - e^{-at}) \qquad (3)$$

Substituting in (3) for t which equals v/r and combining (1) and (3) we have

$$Q = \frac{kv}{av}\tau r(1 - e^{-av/r}) \qquad (4)$$

One may fit the three sets of Q *versus* r values to equation (4) most simply by trial, determining thereby the two parameters av and $kv\tau/av$, from which $kv\tau$ may be determined. Neither the value of τ, which is known, nor the value of v is of importance, since they are constants and it is the relative rates only that are at present of interest.

The expression obtained, assuming a second power dependence for the decomposition, is somewhat more complicated, but proceeding just as above one finds

$$Q = \left(\frac{kv}{av}\right)^{1/2}\tau r\,\frac{1 - e^{-2(ka)^{1/2}v/r}}{1 + e^{-2(ka)^{1/2}v/r}} \qquad (5)$$

Except for the denominator this is of the same form with respect to r as (4), though the two parameters have different meanings. Their product, however, gives $kv\tau$ and their quotient $2av/\tau$. The quantities $kv\tau$ and av of equation (4), termed the relative rate constants of formation and decomposition, are plotted in Figs. 4 and 5.

The results of a series of runs made over the temperature range 250–650°, computed by means of equation (4), are plotted in Fig. 4. A similar series of runs was made at 650° with varying composition of the gas mixture over the range 50–50 to 96–4 in the ratio of nitrogen to oxygen. These results are shown graphically in Fig. 5. The rates of formation and decomposition of oxidized nitrogen are given separately in the two

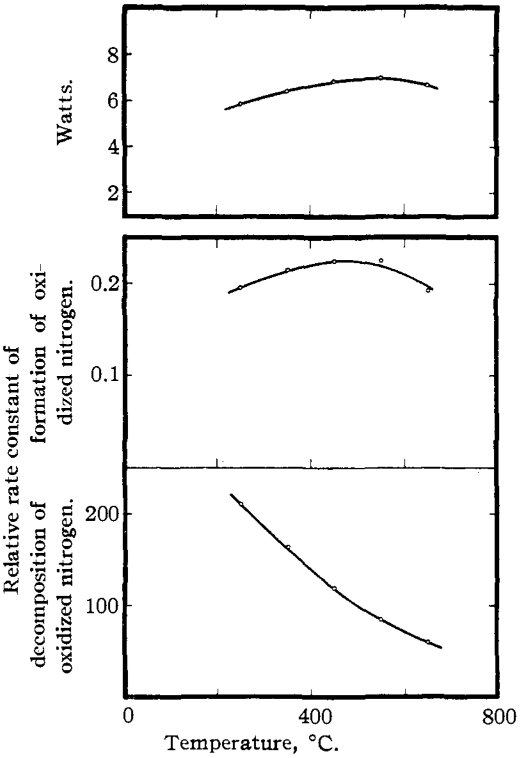

Fig. 4.—Gas mixture–air.

lower portions of Figs. 4 and 5. In the upper section of each figure the power, which was not strictly constant over the measurements, is shown in order to permit an estimate of the extent to which this might have affected the two rates. It may be that, in Fig. 4, the small apparent change in the rate of formation with temperature was chiefly due to the corresponding small change in the power.

Discussion

The data of Fig. 4 indicate that, for the fused quartz ozonizer with which the results were obtained and which was exhibiting remarkably consistent behavior over the weeks in which these data were taken, the rate of formation of oxidized nitrogen varies but little with temperature over the range 250–650°. The rate of decomposition, however, decreases rapidly with increasing temperature.

These two circumstances would explain the marked increase with temperature of the yield of oxidized nitrogen at any one rate of flow, the behavior exhibited in Fig. 2. They would, however, require that this temperature dependence should become less for higher rates of flow, since with a shorter time of stay in the ozonizer the decomposition reaction makes itself less felt on the yield. This behavior may also be seen in Fig. 2, the rate of increase of the yield with temperature being much less at 700 cc./min., for example, than at 100 cc./min. This is clearly seen if the points are considered in terms of the fraction of the yield obtainable at indefinitely high rate of flow, the several curves, from this point of view, coming together rapidly with increasing temperature.

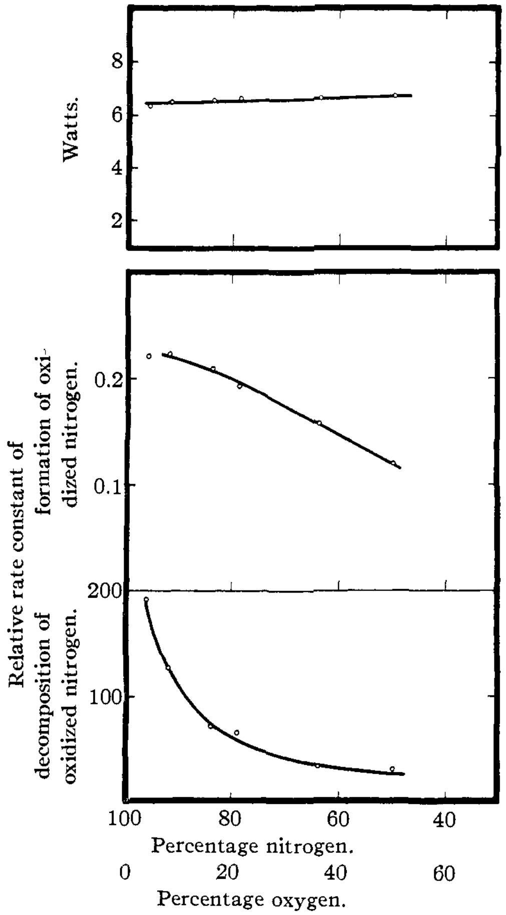

Fig. 5.—Temperature 650°.

At 650° and with respect to the composition of the entering nitrogen–oxygen mixture the results, shown in Fig. 5, indicate a gradual decrease of the rate of formation with increasing oxygen content of the gas, and a rapid decrease of the rate of decomposition over the same range of gas composition. These circumstances are in accord with the results shown in Fig. 3, that an optimum composition exists at which the yield is a maximum for some one rate of gas flow, and that this composition shifts with increasing rate of flow toward higher nitrogen.

Thus the data all tend to indicate that over the temperature range 200–800° and with change of the nitrogen–oxygen ratio of the gas mixture no large change occurs in the rate of formation of oxidized nitrogen in the ozonizer discharge, but that the rate at which the oxidized nitrogen is broken up by the discharge varies greatly with these two factors, accounting for the fact that at any one rate of gas flow marked variations in the yield may be found when these two factors are varied. It is interesting in this connection to compare these results with those of Brewer and collaborators[8] obtained in the glow discharge.

The temperature range over which the present results were obtained is suggestive of the equilibrium

$$NO_2 = NO + {}^1/_2O_2$$

The behavior observed suggests that the rate of decomposition of the oxidized nitrogen may be proportional to the amount of nitrogen dioxide existing in the gas. The fractional oxidation of nitrogen dioxide as a function of temperature for an oxygen pressure of one-fifth of an atmosphere is shown in Fig. 6, computed from data in "International Critical Tables," Vol. VII, p. 239. It is clear that this falls approximately as does the rate of decomposition of the oxidized nitrogen shown in Fig. 4. That nitrogen dioxide might be effective in promoting the decomposition of oxidized nitrogen by the discharge is suggested by the well-known observation at room temperature of the "ozoneless" discharge occurring when very small amounts of nitrogen dioxide are present in the gas. Ehrlich and Russ[9] have studied the marked influence which small amounts of nitrogen dioxide have upon the breakdown potential and upon the potential across the gas space in nitrogen–oxygen mixtures.

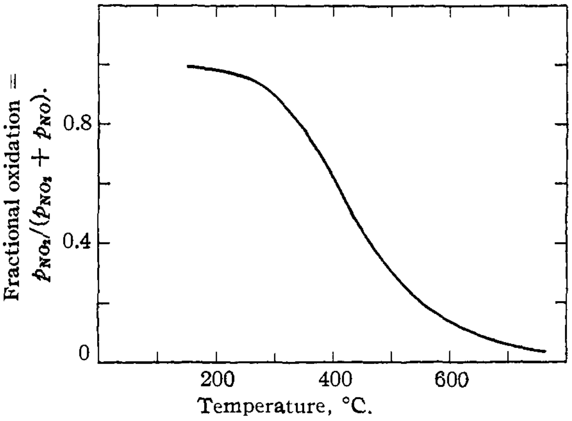

Fig. 6.

It is difficult to suggest an explanation for the behavior with changing nitrogen–oxygen ratio at 650° shown in Fig. 5. The moderate decrease of the rate of formation with increasing oxygen content is in qualitative accord with the behavior observed in the glow discharge[8] and may be explained, as it was in that work, as due to the circumstance that the formation is caused only by the action of the discharge on nitrogen. However, the very rapid decrease of the rate of decomposition with increasing oxygen content seems characteristic of these pressures and temperatures since it was not observed in the glow discharge. It would appear that in the ozonizer discharge, oxygen, or some other constituent whose existence is dependent upon the presence of oxygen, acts strongly to inhibit the decomposition under these conditions.

A number of separate observations were made in the high temperature range 650–1000°. These substantiated the rapid decrease of the yield above 800–850°, shown in Fig. 2. The yield at 1000° varied somewhat. It was not always quite zero, due perhaps to small fluctuations in the behavior of the ozonizer or to the circumstance that the yield is sensitive to small differences in temperature at this point. In every instance, however, the yield at 1000° was very low.

At this temperature, however, the homogeneous thermal decomposition of nitric oxide possesses too low a rate to be the cause of this low yield, and it seemed also probable that no catalytic thermal reaction in the ozonizer would be sufficient.[10] To make certain of this, a second water-cooled ozonizer was placed in the system before the quartz ozonizer, and observations were made of the yield when the water-cooled ozonizer was in operation, but the quartz ozonizer was simply held at 1000° and not in electrical operation. No decomposition of oxidized nitrogen was observed in this passage of the gases through the quartz ozonizer at 1000°, thus showing that the drop in the yield around 1000° when the quartz ozonizer was operating was not due to the thermal decomposition of nitric oxide.

The data of Fig. 2 at 900° indicate that the

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(8) Brewer and Kueck, *J. Phys. Chem.*, **37**, 889 (1933); Westhaver and Brewer, *ibid.*, **34**, 554 (1930).

(9) Ehrlich and Russ, *Monatsh.*, **36**, 317 (1915).

(10) Jellinek, *Z. anorg. Chem.*, **49**, 229 (1906).

rapid drop in yield in this region is due to a decrease in the rate of formation in the discharge and not to an increase in the rate of decomposition. An observation confirming this was made subsequent to those just described. It has been stated that with the water-cooled ozonizer operating and the quartz ozonizer held at 1000° but not in electrical operation, the yield was uninfluenced by the quartz ozonizer. When now the discharge was thrown on the quartz ozonizer also, that is to say, both ozonizers put in operation, the yield of the first was not decreased by passage through the second but was slightly increased, indicating that the discharge of the 1000° quartz ozonizer was not decomposing in any great extent the considerable quantities of oxidized nitrogen entering it, but, rather, adding very slightly to these and in amount such as might be expected from the operation of this ozonizer alone. It therefore seems probable that in the vicinity of 1000° a marked decrease in the rate at which oxidized nitrogen is being formed in such an ozonizer actually occurs. Unfortunately the present data do not permit determining whether or not this decrease in the rate of formation is simply a decrease in the power taken by the ozonizer, that is, a decrease in the intensity of the discharge due to the increase in the conductivity of the quartz dielectrics. From 800 to 1000° the secondary current increased considerably, the primary current slightly, while the wattmeter indicated a considerable decrease in power. It seems probable that an actual falling-off of the intensity of the discharge in the ozonizer is the explanation of the rapid decrease of the yield in this temperature range.

The authors gratefully acknowledge the assistance and advice received throughout the work from Mrs. L. S. Deming, Dr. E. H. Melvin and Mr. R. A. Nelson.

Conclusions

When air is passed at a constant rate through a quartz ozonizer, the temperature of which is raised from 200° to about 800°, the yield of oxidized nitrogen increases with the increase of temperature, but this increase is a function of the rate of flow and is less at the higher flows.

At 650° the yield of oxidized nitrogen varies with the nitrogen–oxygen ratio of the gas flowing through the ozonizer, the yield passing through a maximum that lies in the region of high nitrogen ratios. The position of the maximum, however, is a function of the rate of flow and is displaced toward higher nitrogen ratios with increasing flow, the yield at the maximum and at any other one ratio increasing at the same time.

Analysis of the results of measurements over the temperature range 250–650°, made to determine separately the rate of formation and rate of decomposition of oxidized nitrogen in the ozonizer, shows that the rate of formation does not change greatly but that the rate of decomposition decreases rapidly over this temperature range. This latter accounts for the increase of yield with temperature.

Similar analysis based on the results of measurements for a series of nitrogen–oxygen ratios at 650° shows that while the rate of formation of oxidized nitrogen increases slowly with increasing nitrogen–oxygen ratio, the rate of decomposition also increases and in particular increases very rapidly as the gas mixture approaches pure nitrogen. It is this circumstance that accounts for the maximum in the yield with changing nitrogen–oxygen ratio, and for the displacement and increase of the maximum with increasing gas flow.

Up to about 800° in a quartz ozonizer rendered stable through long operation the pure rate of oxidation varies relatively little with changes in temperature and in the nitrogen–oxygen ratio. The large variations in this rate which do frequently occur in an unconditioned ozonizer with time and with change of temperature arise from changes in the dielectric surfaces between which the many minute discharges, comprising the ozonizer discharge, occur. Recent work on the physical character of such discharges seems to afford an explanation for such variations.

Above 800° the yield of oxidized nitrogen falls rapidly, becoming very small in the vicinity of 1000°. Though in the present work the data obtained over this temperature range are less adequate than those for temperatures below this, there is indication that over this high temperature interval and in such an ozonizer the rate of oxidation itself decreases rapidly.

WASHINGTON, D. C.

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