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Chemical Reaction in Silent Electric Discharge. I.
The Mechanism of Ozone Formation

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The ozone formation reactions in the silent electric discharge starting from oxygen under atmospheric pressure and varied electric conditions were investigated. The results were found to be in line with the theory based on the postulates of reactional and electrical pattern, proposed earlier by authors. The reaction regime in discharge columns where the main reactions proceed is unusual. The duration of high frequency discharge which initiates the primary reactions is extremely short compared to the apparent duration of discharge of basic primary current. Thus, in the discharge columns a non-steady reaction regime is established. A rate theory is developed for the processes in silent discharge based on a non-steady state assumption, which is acceptable in view of the experimental results. The proposed pattern of processes is useful for obtaining more detailed mechanism of the reaction involved.

Ozone formation in silent electric discharge has been a richly productive research project[1,2] for many years both from pure chemical and technical, as well as electrical viewpoints. Nevertheless, several points in the reaction mechanism, above all the dependence of the reactions on electrical processes, still remain unclarified.

The authors have tried to explain the experimental results without using a steady state assumption. It does not seem appropriate to apply this assumption to the silent discharge reaction regime of the present type, which is remarkably different from ordinary gas phase reactions.

The earlier proposed postulate is briefly summarized below.

1. The primary reaction is initiated by electrons in a high frequency electric field established by discharge due to the applied base potential of a low frequency current of 50 Hz of city source[1].

2. The rate of initiation reaction is proportional to the electric quantity, or the number of electrons, passing through the discharge space during a certain period, such as half cycle of low frequency current.

3. The discharge essentially takes place through numerous tiny columns strewn across the entire discharge space which are perpendicular to both electrode surfaces. In other words, the discharge space between the electrodes is divided into two regions,; one, the discharge columns through which displacement currents flow, and the other, the discharge free zone which is essentially free from electrons during and also after discharge.[1]

4. The number of discharge columns which are visibly observable, for instance, on photographic plates eventually serving as alternates of electrodes, is proportional to the total displacement current passing through the discharge columns under similar conditions.[1]

5. The sites of initiation reaction are then the space within the discharge columns, and further reactions will proceed either in discharge columns exclusively, or both in discharge columns and in discharge free zone according to the nature of individual chemical reactions and to the surrounding and ambient conditions.

Experimental

1. The device for the electric discharge and the flow system for the reactions were essentially similar to those described.[1] The block diagram and specifications are given in Fig. 1.

The discharge vessel or the ozonizer used was of a plate type (Fig. 2). The area of electrode, viz., the area of the copper foil pasted outside both electrodes which face each other parallel and congruently, was 37.5 cm^2, and the space gap between the electrodes was 1.25 mm for almost all runs. The pressure was maintained at 1 atm. in the ozonizer.

The reactions were highly sensitive to the chemistry and geometry of the reaction system as well as to electricity, which sometimes showed poor reproducibility of the measurements. Thus, the physical conditions, such as electrode material, thickness, nature of elec-

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[1] M. Suzuki, *Proc. Japan Acad.*, **26**, 21 (1950); M. Suzuki and Y. Naito, *ibid.*, **28**, 429 (1951); M. Suzuki, S. Okazaki and T. Yamamoto, *J. Amer. Chem. Soc. Advan. Chem. Ser.*, **26**, 331 (1957); K. Morinaga and M. Suzuki, This Bulletin, **34**, 157 (1961); *ibid.*, **35**, 204, 429 (1962); von A. Klemenc, H. Hintenberger and H. Höfer, *Z. Elektrochem.*, **43**, 708 (1937).

[2] K. Honda and Y. Naito, *J. Phys. Soc. Jap.*, **10**, 1007 (1956); J. C. Devins, *J. Electrochem. Soc.*, **103**, 460 (1956); T. C. Manley, *Trans. Elektrochem.*, **84**, 83 (1943).

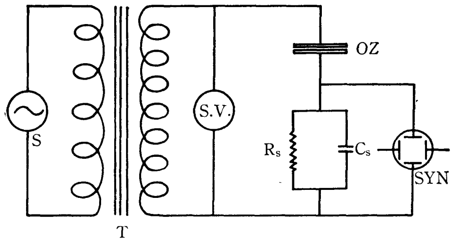

Fig. 1. Block diagram of measuring system.

S: A. C. source, 100 V, 50 Hz
T: Step-up transformer
S.V.: Static voltmeter
OZ: Ozonizer
Rs: 3 kΩ
Cs: 5300 pF
SYN: Synchroscope

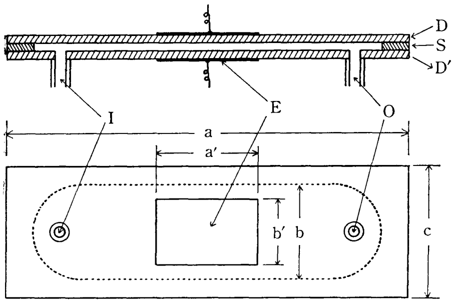

Fig. 2. Parallel plate ozonizer.

Ozonizer scales;
Whole size: a(=400 mm) × c(=100 mm).
Inside of dotted line: gas mixture streaming space, b=68 mm.
E: Cu-foil electrodes a'=75 mm, b'=50 mm.
I, O: in and outlet of gas mixture.
D=D': glass electrodes, 1.25 mm thick.
S: glass spacer, 1.25 mm thick.

trode surface, and the geometry of the experimental details or individual measurement gadgets, were kept as consistent as possible in order to eliminate cumber.

2. An optical method was employed for analysis of the produced ozone. The ozone concentration in down stream gas mixture was automatically recorded, while the absorption of 2540 Å line of ozone was continuously measured by a spectrophotometer, Hitachi EPU 2A Type, combined with a micro recorder, Hitachi QPD 33 Type. Validity of the recording scale was calibrated using the values of chemical analysis, which was found to be within 0.1% error.

3. The high frequency displacement current was sometimes unsteady and inreproducible. The electrical items involved in the measuring system were controlled with contingent precautions for each series of runs.

The high tension voltage (V) applied to the discharge system was measured by a static voltmeter (Fig. 1). The indicated values on the voltmeter gave the values of electric potential with which the condenser system (Cs and OZ in Fig. 1) should be charged. The actual field strength along the discharge path during the high frequency discharge is not yet clearly known, but some useful informations are available. The relations among various electrical quantities, such as the values of applied potential on individual condenser and the quantity of electricity were extensively discussed by Miura and Kawai.[3] This was of help in the estimation of various electric quantities from directly measured values, in spite of little knowledge of the field strength in the discharge columns.

The quantity of electricity (Q) transferred through the electrodes during a half cycle of primary base current governs the processes of chemical reactions, above all the initiation reactions originated in discharge columns.

The length of each hair[1] *i.e.* the pulse current on an oscillogram monitor of a half cycle of 50 Hz base current (Fig. 8) represents the high frequency current passing through discharge columns. From the summation of the lengths of these individual hairs the value of Q could be estimated.[1,3]

A synchroscope Iwasaki SS-5004 was used for the monitoring of discharge patterns. The indicated scale values on the gadget were taken to be valid.

Specifications of the electrical equipments were checked to ensure elimination of any possible irreproducibilities. Air or oxygen was used in the streaming gas mixture, though in the present investigation air was almost entirely used, because the theoretical treatment did not differ much for the two gas mixtures.

Results

1. Relation between the Applied Voltage and the Quantity of Electricity. The quantity of electricity carried through parallel plate electrodes is a linear function of the applied voltage on the electrodes. The slope of a straight line

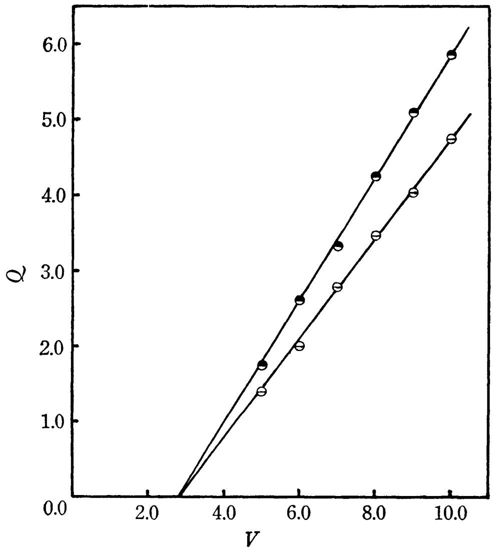

Fig. 3. Relations between quantity of electricity, Q(10^{-7} coulombs) and applied voltage, V (KV).
⊖: F=2.09 cm^3 sec^{-1}.
◓: F=14.26 cm^3 sec^{-1}.

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[3] R. Miura and T. Kawai, *Kogakubu Kenkyu Hokoku (Reports on Scientific Researches), Hokkaido Univ. Eng. Dept.* No. 15, 142 (1956).

related to both quantities is governed virtually by the value of the electric constants of the discharge circuit. Such relations were obtained for a wide range of flow velocity variations. The results are shown in Fig. 3.

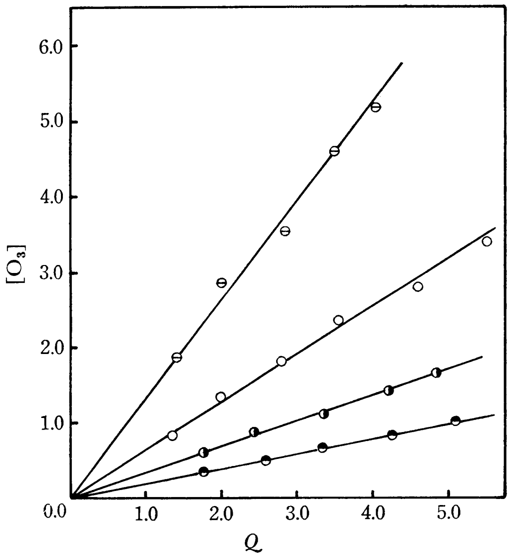

Fig. 4. Relations between quantity of electricity Q(10^{-7} coulombs) and ozone concentration $[O_3]$ (10^{-3}g l^{-1}).
⊖: F=2.09 $cm^3 sec^{-1}$. ○: F=3.88 $cm^3 sec^{-1}$.
◑: F=7.44 $cm^3 sec^{-1}$. ◓: F=14.26 $cm^3 sec^{-1}$.

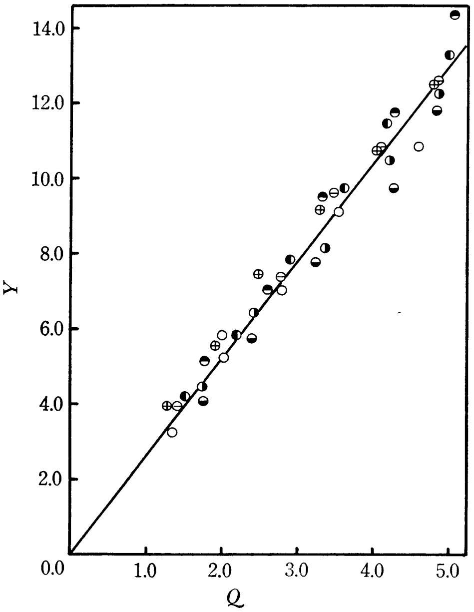

Fig. 5. Relation between quantity of electricity Q (10^{-7} coulombs) and ozone yield Y (10^{-6}g· sec^{-1}).
⊕: F=1.69 $cm^3 sec^{-1}$. ⊖: F=2.09 $cm^3 sec^{-1}$.
○: F=3.88 $cm^3 sec^{-1}$. ◐: F=5.59 $cm^3 sec^{-1}$.
◒: F=6.67 $cm^3 sec^{-1}$. ◑: F=7.44 $cm^3 sec^{-1}$.
◓: F=14.26 $cm^3 sec^{-1}$.

2. Ozone Formation and Electrical Quantities. The results obtained are summarized in Table 1. In Fig. 4 the concentrations of ozone $[O_3]$ (10^{-3} g l^{-1}) in the exit gas mixture from the discharge vessel are shown against the quantity of electricity Q (10^{-7} coulombs during a half cycle of base current) for various flow velocities F(cm^3 sec^{-1}). The slopes of straight lines in sequence, each of which refers to a certain flow velocity, increase almost in proportion to the decrease of the flow velocity. The relation shows that the final ozone concentration after passing through the successive discharge columns is virtually inversely proportional to the flow velocity. The quantity $F\times[O_3]$, which is in turn the ozone yield Y (10^{-6} g sec^{-1}) *vs.* Q should be expressed then as a single straight line irrespective of the flow velocities, which vary to as much as ten times (Fig. 5).

In Fig. 6 similar lines for O_3 *vs.* V are shown.

Table 1. Summarized results

F $cm^3 sec^{-1}$	V kV	Q 10^{-7} coulombs	$[O_3]$ 10^{-3} g l^{-1}	Y 10^{-6} g sec^{-1}
1.69	5.0	1.27	2.35	3.97
	6.0	1.92	3.33	5.63
	7.0	2.49	4.42	7.47
	8.0	3.29	5.44	9.19
	9.0	4.04	6.39	10.80
	10.0	4.79	7.41	12.52
2.09	5.0	1.40	1.88	3.93
	6.0	1.99	2.80	5.85
	7.0	2.80	3.54	7.40
	8.0	3.48	4.60	9.61
	9.0	4.04	5.17	10.81
	10.0	4.74	5.98	12.50
3.88	5.0	1.35	0.83	3.22
	6.0	2.01	1.35	5.24
	7.0	2.80	1.81	7.02
	8.0	3.54	2.35	9.12
	9.0	4.61	2.80	10.86
	10.0	5.51	3.40	13.19
5.59	5.0	1.52	0.75	4.19
	6.0	2.20	1.05	5.87
	7.0	2.92	1.40	7.83
	8.0	3.60	1.74	9.73
	9.0	4.17	2.05	11.46
	10.0	5.00	2.38	13.30
6.67	5.0	1.76	0.61	4.07
	6.0	2.41	0.86	5.74
	7.0	3.25	1.17	7.80
	8.0	4.27	1.46	9.74
	9.0	4.85	1.77	11.81
	10.0	6.13	2.09	13.94
7.44	5.0	1.75	0.60	4.46
	6.0	2.43	0.86	6.40
	7.0	3.36	1.10	8.18
	8.0	4.22	1.41	10.49
	9.0	4.85	1.65	12.28
	10.0	5.85	2.03	15.10
14.26	5.0	1.77	0.360	5.13
	6.0	2.61	0.496	7.07
	7.0	3.34	0.666	9.50
	8.0	4.27	0.823	11.74
	9.0	5.09	1.01	14.40
	10.0	5.87	1.20	17.11

The features of the lines are similar to those on Fig. 4, which is conceivable from Fig. 3.

3. Flow Velocities and Ozone Yields. The ozone concentration $[O_3]$ is inversely proportional to F as shown in Fig. 7. The diagrams are examples picked up from Table 1. The relations hold within the range given in Table 1.

Discussion

1. Electrical Pattern in Discharge Columns. In the course of ozone formation, the initiating primary step is involved in collisions between oxygen molecules and electrons. The paths of electrons are confined in discharge columns strewn across the discharge space between the two electrodes. Such columns which connect both electrodes electrically could be considered as channels solely through which electrons travel.

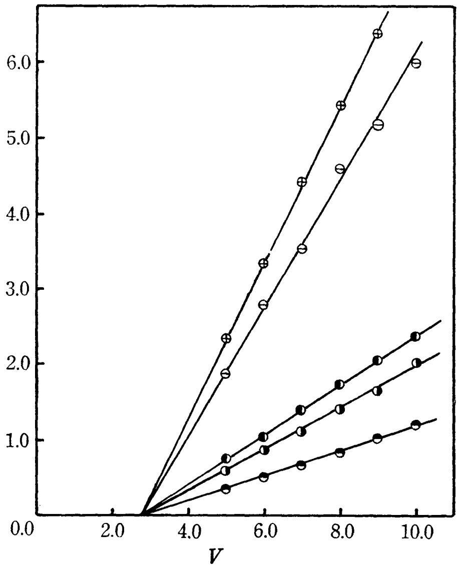

Fig. 6. Relations between ozone concentration $[O_3]$ $(10^{-3}\,g\,l^{-1})$ and applied voltage V (KV). ⊕: $F=1.69\,cm^3\,sec^{-1}$. ⊖: $F=2.09\,cm^3\,sec^{-1}$. ◐: $F=5.59\,cm^3\,sec^{-1}$. ◑: $F=7.44\,cm^3\,sec^{-1}$. ◓: $F=14.26\,cm^3\,sec^{-1}$.

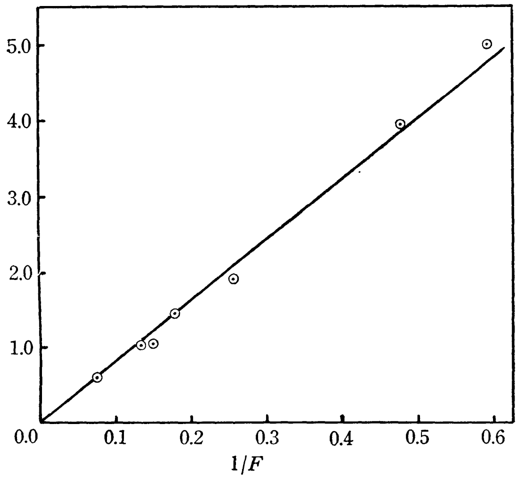

Fig. 7. Relation between ozone concentration $[O_3]$ $(10^{-3}\,g\,l^{-1})$ and reciprocal of flow velocity F $(cm^{-3}\,sec)$.
$Q=3.0\times10^{-7}$ coulombs.

Neither the shape of cross sections of the channels which may be circular, nor their area which may be consistent along the channel from one electrode to the other, is known definitely, though it is almost certain that the channels are perpendicular to both electrode surfaces.

On the other hand, it is known that from the image of discharge columns on a photographic plate which served as a substitute of an electrode, the size of images of each column were found to be fairly equal.[1] The linear dimension at the bottom of columns was less than 1 mm. As the size of the columns is essentially governed by the number of electrons travelling through them, the number of electrons will be fairly consistent in each column. The current density in individual discharge columns is very likely to be constant.

The current flowing through columns is a high frequency one, or a displacement current whose frequency is dependent on the time constants of discharge circuit. Both from the oscillogram and the numerical value of actual electrical items in the measurement system, the oscillation frequency of high frequency current could be estimated to be about 10^6—10^7 Hz. Because of the high resistance of electrode material, the oscillation is highly dampened and only the first one oscillation of the high frequency current was confirmed by oscillogram patterns.[1]

When the applied high potential is gradually raised to a certain definite value, for instance V_1, a discharge or emission of electrons will take place in certain spots on one of the electrodes, which is eventually negative. A glass electrode does not usually have a perfectly flat surface, and there are numerous very small protrusions and indentations all over it. The smaller the radius of curvature r_1 of a very small protrusion, the easier the advent of a discharge from the protrusion, because the

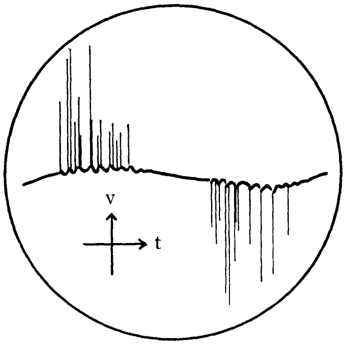

Fig. 8. Synchroscope monitoring of the pulse current (hairs) on primary current wave form.

smaller the r_1 the larger the field strength.

In Fig. 8 which shows the pulse current, the applied voltage (base line) increases from left to right, though the rise is not very distinct because of the deliberate suppression of ordinate scale. Each hair corresponds to pulse current corresponding to a certain value of applied voltage V_1. The pulse current is the sum of each individual pulse current originating from the protrusions whose radii of curvature are r_1. The pulses from left to right correspond to the protrusions for increasing r_1, corresponding to the increase of voltage which enables a discharge from the protrusions. In the other half cycle of base current analogous processes in opposite direction will take place. The high frequency discharge is actually realized only once from the same spot during course of the half cycle of basic current.

2. Reaction Mechanism in Discharge Regime. The proposed reaction sequence of ozone formation in silent discharge is as follows

$$\mathrm{O_2} + e \xrightarrow{k_0} \mathrm{O} + \mathrm{O} + e \qquad (0)$$

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{O_3} + \mathrm{M} \qquad \begin{matrix}(1)\\(-1)\end{matrix}$$

$$\mathrm{O_3} + e \xrightarrow{k_2} \mathrm{O_2} + \mathrm{O} + e \qquad (2)$$

$$\mathrm{O_3} + \mathrm{O} \xrightarrow{k_3} \mathrm{O_2} + \mathrm{O_2^*} \qquad (3)$$

$$\mathrm{O} + \mathrm{O} + \mathrm{M} \rightarrow \mathrm{O_2} + \mathrm{M} \qquad (4)$$

$$\mathrm{O_2} + \mathrm{O_2^*} \rightarrow \mathrm{O} + \mathrm{O} + \mathrm{O_2} \qquad (5)$$

where e is electron, and M could be either oxygen or nitrogen. For the sake of simplicity M is treated here exclusively to be oxygen because the effectiveness of both molecules in the reactions does not essentially show much difference.[4] Some of the values of k were estimated.

$$k_1 = 6.0\times 10^7 \exp\,(+0.6/\boldsymbol{RT})\ l^2\,\mathrm{mol}^{-2}\,\mathrm{sec}^{-1}$$ [4,5]

$$k_{-1} = (4.61\pm0.25)\times 10^{12}\ \exp\,(-24.4/\boldsymbol{RT})\ l\,\mathrm{mol}^{-1}\,\mathrm{sec}^{-1}$$ [5,6]

$$k_3 = (3.0\pm0.3)\times 10^{10}\ \exp\,\{(-6.0\pm0.7)/\boldsymbol{RT}\}\ l\,\mathrm{mol}^{-1}\,\mathrm{sec}^{-1}$$ [6]

Reactions (3) and (4) are negligible because of the low concentration of O atoms and $\mathrm{O_3}$ molecules, and reaction (5) was discarded[7] because of its eligibility only at high temperatures. Finally reaction (−1) could be put aside[4] at room temperature, which is essentially the temperature of the discharge vessel. Because of very short and intermittent advent of discharges, essentially any considerable temperature enhancement in the discharge vessel could hardly be perceptible. Thus the reactions (0), (1) and (2) are of practical interest in this reaction regime. The reaction (0) or the initiation reaction will proceed solely in discharge columns. The duration of high frequency current through columns is 10^{-6}—10^{-7} seconds. The electron drift velocity depends on E/p value in the discharge vessel, where E is the value of potential gradient (volt cm^{-1}) between the electrodes and p is the ambient pressure (mmHg), from which E/p is far less than unity.[8] In consideration of this value, the electron drift velocity could be estimated to be about 10^6—10^7 cm sec^{-1}. If the linear flow velocity of gas mixture is taken to be 10 cm sec^{-1}, and diameter of the discharge column to be 0.5 mm in average, then the resident time of gas mixture whithin a discharge column is about 5×10^{-3} sec. Now the number of columns through which streaming gas mixture passes is inversely proportional to its flow velocity. The number of electrons which shower on the gas mixture is proportional to the number of columns. Thus we conclude that the number of oxygen atoms produced by reaction (0), which in turn produced ozone molecules, should be roughly inversely proportional to the flow velocity. As the experimental results show, the ozone concentration of a certain gas mixture is really inversely proportional to the flow velocity (Fig. 7) under similar conditions.

A more detailed insight of the reaction mechanism will be discussed in the following section.

3. The Reaction Pattern based on a Non-steady State Assumption. In silent discharge both from spacial and time-resolved viewpoints three types of reaction regime could be designated: **A**$_1$) reactions going on in any discharge column within the time of high frequency discharge, during which the electrons reside in the column and their resident time is about 10^{-6}—10^{-7} sec; **A**$_2$) reactions going on in any discharge column within the interval between any two successive high frequency discharges which is 10^{-2} sec or a half cycle of base current, where any electrical phenomena are precluded; and **B**), reactions going on in the space outside discharge columns during the resident time of reaction gas mixture in the discharge vessel.

These three types of reaction regime will be discussed individually.

A$_1$: this is a reaction regime where electrons participate. The density of electrons will be larger on account of the smallness of the volume

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[4] W. M. Jones and N. Davidson, *Abstracts of Papers, 135th Meeting, Amer. Chem. Soc.*, p. 37 R. (1959).

[5] S. W. Benson and A. E. Axworthy, Jr., *J. Chem. Phys.*, **26**, 1718 (1957).

[6] F. Leighton, H. B. Urbach, J. A. Wojtowicz and J. A. Zaslowsky, *Abstracts of Papers, 136th Meeting, Amer Chem. Soc.*, p. 46 S. (1959); H. B. Urbach, R. J. Wunk, J. A. Wojtwicz and J. A. Zaslowsky, *ibid.*, p. 47 S. (1959).

[7] R. E. Dugg, *Phys. Fluids*, **1**, 242 (1958); W. Jost, *7th. Combus Symp.*, p. 190 (1959).

[8] R. A. Nielsen and N. E. Bradbury, *Phys. Rev.*, **49**, 338 (1936), **51**, 69 (1937); R. A. Nielsen, *ibid.*, **50**, 950 (1936); R. H. Healey and J. W. Reed, "The Behaviour of Slow Electrons," Amalgamated Wireless Press Ltd., Sydney (1941), p. 94.

of columns compared to the whole discharge space, and it will tend to be smaller as the electron velocity becomes faster (up to 10^7 cm sec^{-1}).[9] The actual value of the electron concentration in the discharge columns in the present investigation is roughly estimated to be about 10^{-10}—10^{-11} mol l^{-1} during the course of high frequency discharge.

The site of reaction (0) is exclusively in the discharge columns, the produced O atoms may react according to reactions (1) and (3), but some part may flow out of the columns along with the gas stream. The electrons will play roles in reactions (0) as well as in (2). Ozone will be produced through reaction (1) and destroyed by reactions (2) and (3), and finally washed out from the columns as O atoms.

Based on a non-steady state assumption, reactions (0), (1), (2), (3) and washing out effect will be expressed in the following way, reaction (—1), (4), (5), *etc.* being discarded.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ay - Bx - Fx \qquad (\mathrm{A_1}\text{-}1)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -Ay + Bx - Fy + C, \qquad (\mathrm{A_1}\text{-}2)$$

where $x=[\mathrm{O_3}]$ mol l^{-1}, $y=[\mathrm{O}]$ mol l^{-1} and $A=k_1[\mathrm{O_2}]^2$. In this case $A=1.1\times10^4\,\mathrm{sec}^{-1}$ at 300°K and at 760 mmHg.[5] Also $B=k_2[\mathrm{e}]$, in which case [e], the electron density, is about 10^{-11} mol l^{-1}, and k_2 mol^{-1} l sec^{-1} is unknown, although from various viewpoints B is most likely less than A. In addition $C=2k_0[\mathrm{O_2}][\mathrm{e}]$, where k_0 is presumably 10^6—10^8 mol^{-1} l sec^{-1}, [10] although the exact value is not estimated. Finally, F is flow velocity (sec^{-1}) which is taken to be $10^{-2}\,\mathrm{sec}^{-1}$. F in Table 1 and Figs. 3—7 is expressed in volume velocity, whereas in this section F times concentration represents the quantity carried by flow. Although the Eq. ($\mathrm{A_1}$-2) is often assumed to be zero, in the present postulate it should most likely remain finite in $\mathbf{A_1}$ regime. The above two equations could then be reduced to

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + Q\frac{\mathrm{d}x}{\mathrm{d}t} + Px - AC = 0, \qquad (\mathrm{A_1}\text{-}3)$$

where $P=(A+B)F+F^2=(A+B)F$ and $Q=A+B+2F=\mathrm{A+B}$. Eq. ($\mathrm{A_1}$—3) is so simple that its general solution is obtained directly under consideration of boundary conditions. Thus we get the final result

$$Px_0 = AC[1 - \exp(-Qt_0)] \qquad (\mathrm{A_1}\text{-}4)$$

where t_0 is the duration of high frequency oscillations, x_0 is the ozone concentration at t_0 or at the stage of reaction at the moment when the high frequency discharge is extinguished. In the course of solving the equations, a physically more suitable complementary root of the characteristic equation is selected. All the right hand side terms of ($\mathrm{A_1}$—4) are independent of flow velocity, but P is proportional to it. Thus x_0 is inversely proportional to the flow velocity.

$\mathbf{A_2}$: In discharge columns after the high frequency discharge terminated, O atoms will still react according to reaction (1) and continue to flow away in the outer zone. Similarly $\mathrm{O_3}$ molecules will be produced by reaction (1) and flow out in the same manner as O atoms. Electrons play no roles here.

Then the tentative equations will be

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ay - Px \qquad (\mathrm{A_2}\text{-}1)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -Ay - Fy \qquad (\mathrm{A_2}\text{-}2)$$

which can be solved easily. The solution is

$$\begin{aligned} x_1 &= [x_0+y_0\{1-\exp(-At_1)\}]\exp(-Ft_1) \\ &\fallingdotseq (1-Ft_1)(x_0+y_0). \qquad (\mathrm{A_2}\text{-}3) \end{aligned}$$

Because of $1\gg Ft_1$, it will further be changed into

$$x_1 \fallingdotseq x_0 + y_0, \qquad (A_2\text{-}4)$$

where t_1 is the duration which is a half period of basic current or 10^{-2} sec., and x_1 is the ozone concentration at the beginning of another overtaking high frequency discharge.

The value of y_0 or [O] at the termination of $\mathbf{A_1}$ regime can be calculated from ($\mathrm{A_1}$—1) and ($\mathrm{A_1}$—4), which gives

$$\begin{aligned} y_0 &= (C/P)[(A+F)\exp(-Qt_0) + (B+F)] \\ &\fallingdotseq (C/P)[A\exp(-Qt_0)+B]. \qquad (\mathrm{A_2}\text{-}5) \end{aligned}$$

In a similar way as discussed in the foregoing section, the terms in the bracket on the right hand side of ($\mathrm{A_2}$—5) are free from F, while P is proportional to F, y_0 is then inversely proportional to F. Thus the $[\mathrm{O_3}]$ value at the termination of $\mathbf{A_2}$ is, as in $\mathbf{A_1}$, proportional to $1/F$. Furthermore, the fact that the value of x_1 in ($\mathrm{A_2}$—4) is almost equivalent to (x_0+y_0) shows that, almost all O atoms react into $\mathrm{O_3}$ molecules, except those washed out of the columns, which are very small, before the termination of $\mathbf{A_2}$ regime. Thus it may be concluded that the ozone formation in the zone outside of columns is very small.

B: Outside the discharge columns, O atoms and $\mathrm{O_3}$ molecules are flowing, while they may react, to a very small extent, according to reaction (1). These particles may incessantly flow into and then emerge out of discharge columns, but processes in and out will obviously cancel each other, and the effect of flow could be neglected.

The required equations are then

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ay \qquad (\mathrm{B}\text{-}1)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -Ay \qquad (\mathrm{B}\text{-}2)$$

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[9] C. E. Normand, *Phys. Rev.*, **35**, 1217 (1936).

[10] To be published.

and the solution, under the consideration of the boundary conditions is

$$x = x_a + y_a[1 - \exp(-At)] \\ \doteqdot x_a \qquad \text{(B-3)}$$

where x is the value of $[O_3]$ at any time, so long as the gas mixture resides in the discharge zone, particularly outside discharge columns, and x_a and y_a are the $[O_3]$ and $[O]$ at the time when the gas mixture is streaming out of a discharge column. The value of y_a is very small (*cf.* $\mathbf{A}_2$). Then x_a is equivalent to x_1 in (A_2—3) and again proportional to $1/F$. It is also conceivable from (B—3) that the extent of ozone formation in space outside discharge columns is very small, as suggested before.

Putting these three reaction regimes together, in $\mathbf{A}_1$ regime where the main part of the reaction proceeds, the ozone concentration is proportional to $1/F$; in $\mathbf{A}_2$ and **B**, where the reactional part of the substrate decreases the produced ozone concentration is again proportional to $1/F$. The experimental results show that the ozone concentration is proportional to $1/F$ for a considerable wide range of flow velocities. This agrees with the proposed theory.

In static system the ozone yield is very low. In very rapid flow where the flow velocity, or the resident time of streaming gas mixture in a column is comparable to the high frequency discharge duration, the reaction pattern should be different from those described above. The values of k_0 and k_3 of reactions (0) and (3) were left unsettled.