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Ignition Delay Time Studies of Hydrogen and Oxygen Reactions through Silent Electric Discharge

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The ignition of hydrogen and oxygen could be induced by the so-called silent electric discharge, and the ignition delay time after the termination of the discharge was found to be proportional to a logarithm of the discharge intensity (pulse current). The proportionality constants in different diluents, argon and helium, were analyzed to yield the net effect of chain breaking in the reaction:

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M$$

and the rate coefficient, k_1, for the reaction:

$$H + O_2 \xrightarrow{k_1} OH + O$$

assuming a third-body efficiency of the diluent gases. It was inferred from the results that the radical reproducing from HO_2 significantly lessened the effect of the above chain breaking reaction, the accumulation of radicals seemed to be persistent even in the low-temperature region, where the k_1 value was observed not to be above the assumed value of $k_1[M]/2$.

The ignition of hydrogen and oxygen by silent electric discharge was reported previously[1] regarding the effects of the gas composition and the pressure on the threshold of the ignition.

The present paper will attempt to estimate the net effect of the chain breaking reaction by com-

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[1] K. Morinaga, This Bulletin, **35**, 627 (1962).

paring the experimental results on the ignition delay time in an argon diluent and in a helium diluent, assuming a third-body efficiency of the diluent gases.

Unlike spark discharge, silent discharge can be characterized by numerous small discharges which continue for a certain period of time. These small discharge can be represented on the Lichtenberg figure[2] as numerous spots[3] sporadically distributed all over the electrode (which is a dielectric substance) surface and on the current diagram as numerous fringe-like pulses the summation of which can lead to pulse current.[3,4] These are essential features of the silent electric discharge.

The linear relationship between the pulse current and the extent of chemical reaction in silent discharge was confirmed in previous papers.[5,6]

In the present paper, the pulse current was adopted in order to show the extent of the discharge which brings about the silent-discharge ignition of hydrogen and oxygen.

Experimental

Hydrogen, oxygen, and inert gases over three-nine pure were dried over silica gel and were then manometrically mixed to the desired composition in a conventional vacuum system without further treatment. The mixture was left to stand for more than 48 hr ($p=1$ atm) in a glass vessel before use. The composition of the inert gas *i. e.*, argon or helium, ranged from 5 to 55%, while the hydrogen and oxygen remained stoichiometric. The initial pressure of the gas mixture for runs was kept at 250 mmHg in all cases.

The electric circuit system which actuated the one-shot silent electric discharge and the device for the observation of the current diagram of the discharge were similar to those in previous experiments.[1,7] Under the present experimental conditions, the pulses on the current diagram appeared satisfactorily separated for convenient pulse-height measurements.

The cylindrical test bomb of the preceding work[1] was replaced by a cubic bomb with a 3 cm×8 cm×8 cm interior. It was provided with a quartz window for observing the emission from the ignited gas. The former conventional spark plugs[1] through which a high voltage was applied to the inside electrodes were replaced by Teflon plugs for better insulation from surface leakage. A safety diaphragm and needle valves were attached to the bomb just as in the previous work. The leak rate of the bomb system was less than 2 mmHg per hour in any case, and the bomb was filled with the test gas after repeated washing operations which took less than 3 min.

The silent discharge electrodes were composed of two polished Toshiba Terex glass plates (hard glass of the boric oxide type) 5 cm×6 cm×1 mm. The discharge gap distance of the electrodes was maintained by means of cementing an appropriate glass piece in each corner of the plate, and the discharge gap width was within the limit of 2.05—2.12 mm. Tin foil (7.5 cm²) was stuck on the outside of the glass electrodes. The entire set-up of the electrodes was sustained by two springs which acted as electric leads insulated from the test bomb by the Teflon plugs.

The pick-up system for the emission from the ignited gas between two electrodes consisted of two slits, an interference filter,[*1] and a photomultiplier tube (RCA 1P-28). The slits were designed so as not to transmit any light from the electrode surface. The interference filter separated the band system of $OH(^2\Sigma-{}^2\Pi)_{v=0,0}$ from the other emission of the ignited gas. The signal from the photomultiplier tube and the current diagram of the discharge were recorded simultaneously on a dual-beam oscilloscope.

To avoid unnecessary disturbance of the light-emission trace due to the discharge noise, much care was taken and all the ground points were coordinated at a unified earth point while the test bomb was floating, entirely from the ground.

A primary DC current was applied to the primary coil of a transformer through a switch, the ON and OFF operation of which produced secondary high tension in the secondary circuit. The discharge intensity or the pulse current in the secondary circuit could be regulated by changing the primary DC current, while the discharge period was less affected. In the present experiment, the high tension in the secondary coil which accompanied the ON stage of the switch was used exclusively.

Results

Typical oscillographic patterns of the pulse current and of the signal from the photomultiplier tube are shown in Fig. 1, where t and τ_i denote the discharge period and the ignition delay time

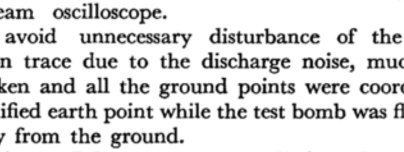

Fig. 1. Oscillographic pattern of current diagram (upper trace) and OH emission profile (lower trace).
t, discharge period; τ_i, ignition delay time; $[OH]_i$, a certain definite concentration of $OH(\Pi)$.

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2) G. L. Lichtenberg, *Novi. Comment Gött.*, **8**, 168 (1777); Y. Toriyama, "Dust Figure of Surface Discharge and its Applications" (in English), Kinokuniya, Tokyo, Japan (1961).

3) M. Suzuki and Y. Naito, *Proc. Japan Academy*, **28**, 469 (1952).

4) K. Honda and Y. Naito, *J. Phys. Soc. Japan*, **10**, 1007 (1955).

5) K. Morinaga and M. Suzuki, This Bulletin, **34**, 157 (1961); **35**, 204, 429 (1962).

6) K. Morinaga, *ibid.*, **35**, 345, 625 (1962).

7) K. Morinaga and M. Suzuki, *Memoirs of the Defense Academy*, VII, 1031 (1967).

[*1] Baird Atomic, Inc., U. S. A., A-31; Peak, 3070 Å; Half Peak Band Width, 100 Å.

respectively. The ignition delay time is determined by two cut-off points, one of which is the termination of the silent electric discharge and the other, the rise of the light emission to a definite value. In the figure, the ordinate of the upper trace can be represented by Coulomb units; the sum of the pulse heights divided by t gives the pulse current, I_p.

With an increasing in the pulse current, the ignition delay time decreased. Figures 2 and 3 show the relation between the ignition delay time and the logarithm of the pulse current in the argon diluent and the helium diluent respectively. The solid lines in the figures represent the least-square

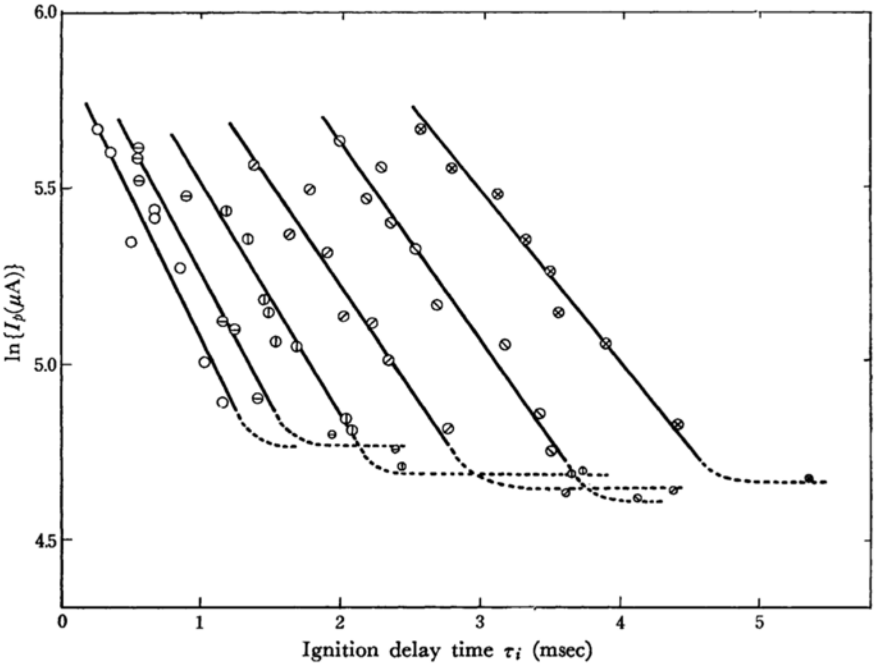

Fig. 2. Relation between ignition delay time and pulse current in argon diluent mixtures. Diluent composition is; ○, 5%; ⊖, 15%; ⦶, 25%; ⊘, 35%; ⦸ 45%; ⊗, 55%.

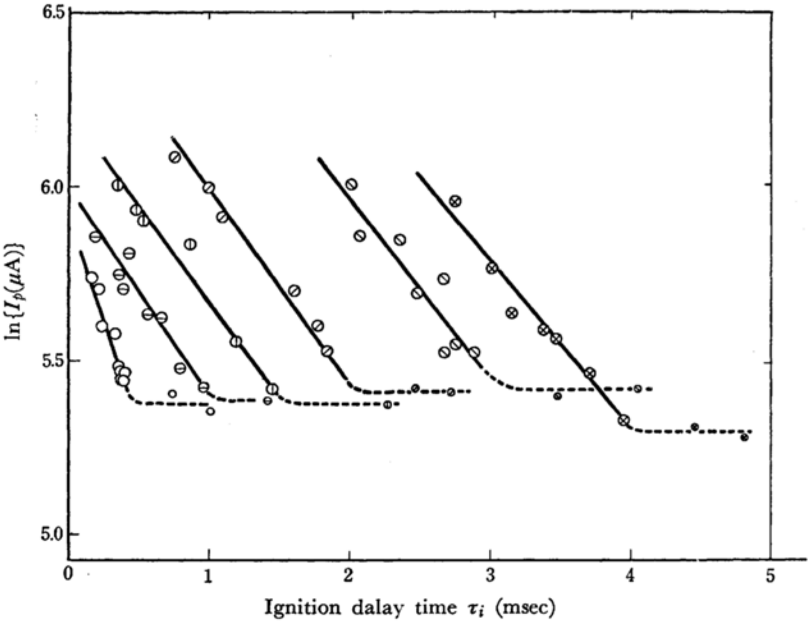

Fig. 3. Relation between ignition delay time and pulse current in helium diluent mixtures. Data points as in Fig. 2.

lines of the experimental results which are shown by the larger circles. The ignition delay time shows a linear relationship against the logarithm of the pulse current well above the threshold of the ignition, though the results most contiguous to the threshold manifest themselves in the longer delay time region, as are shown by the smaller circles.

The threshold pulse current value of the ignition in the helium diluent is of an order of magnitude higher than that in the argon diluent, while the threshold value in argon tends to decrease with an increase in the argon fraction; however, only the difference in the slopes of the solid lines in the argon diluent and the helium diluent will be discussed in the present paper.

To check indirectly whether or not any unexpected corona discharge occurred, electrodes, the outer surfaces and corners of which had been covered by paraffin wax, were tested. However, there was no significant difference in the experimental results between paraffin-coated and non-coated electrodes.

Two photomultiplier experiments, in which one of the photomultipliers was used for the observation of the outer side of the electrodes, and the other, for the inside, were conducted. It was confirmed that the ignition always started from the midst of the electrodes.

Discussion

In the course of the pre-induction period, where the silent electric discharge takes place, the chain-carrier radicals H, O, and OH, will be produced:

$$0)\quad H_2,\ O_2 \text{ and } M \xrightarrow{R_0} H,\ OH \text{ and } O$$

where R_0 denotes the rate of the formation of any specific chain-carrier radicals.

As far as the radical concentration at the termination of the discharge is concerned, the following two cases can be presumed as an approximation. If the discharge period, t, is long enough for the radicals to attain a saturated concentration through the discharge on condition that the forward rate is proportional to the pulse current(6,7) and that the decay of radicals is proportional to the concentration, then the radical concentration at the end of the discharge will be proportional to the pulse current. On the other hand, if the back reaction of decay of radicals can be ignored, then the radicals will accumulate through the discharge period, t, and the radical concentration at the end of the discharge will be proportional to $(R_0\times t)$ or to the pulse current multiplied by t. However, under the present experimental conditions, the discharge period, t, was independent of the pulse current, as was stated formerly; therefore, the radical concentration at the end of the discharge will again be proportional to the pulse current.

Accordingly, we can estimate that the radical concentration at the end of the discharge is proportional to the pulse current, or:

$$[H]_0 \propto [O]_0 \propto [OH]_0 \propto I_p \tag{1}$$

After the termination of the discharge, the reaction profile will be analogous to the shock-initiated induction-period reaction starting from the above radical concentration.

The elementary reaction in the hydrogen and oxygen system which should govern the induction period would appear to be the bimolecular reaction among H, O, OH, H_2 and O_2 and the three-body radical recombination reaction. However, in the present case we disregard the mutual reaction among H, O and OH because the concentrations of such species will be very low compared to those of hydrogen and oxygen during the induction period. Accordingly, we assume the following reaction scheme(8,9):

$$1)\quad H + O_2 \xrightarrow{k_1} OH + O$$

$$2)\quad O + H_2 \xrightarrow{k_2} OH + H$$

$$3)\quad OH + H_2 \xrightarrow{k_3} H_2O + H$$

$$4)\quad H + O_2 + M \xrightarrow{k_4} HO_2 + M$$

Miyama and Takeyama(9) found that the gas-phase reaction of HO_2 came to play an important role in a low-temperature and high-pressure regime shock wave experiment. The fate of HO_2, which should be taken into consideration in the present experimental environment, will be:

$$5)\quad HO_2 + H_2 \xrightarrow{k_5} H_2O_2 + H$$

$$6)\quad HO_2 \xrightarrow[\text{wall}]{K_6} \text{destruction}$$

where K_6 is a function of the electrode dimensions, the diffusion coefficient, and the chain-breaking efficiency.

The steady-state assumptions for the O, OH, and HO_2 radicals will lead to the equation:

$$[H] = [H]_0 \exp[\{2k_1 - k_4[M]K_6/(K_6+k_5[H_2])\}[O_2]\tau] \tag{2}$$

and finally to:

$$[OH] = [OH]_0 \exp[\{2k_1 - k_4[M]K_6/(K_6+k_5[H_2])\}[O_2]\tau] \tag{3}$$

where the origin of time, τ, should coincide with the termination of the discharge and where $[H]_0$ and $[OH]_0$ are the concentrations of H and OH at $\tau=0$. We had adopted the rise of OH emission to a definite value as to be used for a cut off point of the ignition delay time, τ_i.

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8) G. L. Schott and J. L. Kinsey, *J. Chem. Phys.*, **29**, 1177 (1958).

9) H. Miyama and T. Takeyama, *ibid.*, **41**, 2287 (1964).

Belles and Lauver⁽¹⁰⁾ referred to the possibility of using the emitted light as an indication of the progress of the main reaction to allow quantitative comparisons to be made between the induction times measured by following the concentration of the ground state $\mathrm{OH}(\Pi)$ with absorption spectroscopy and those measured by the easier method of observing the emitted light, regarding $\mathrm{OH}(\Sigma)$ as having been formed in the monoradical reaction: $\mathrm{H}+\mathrm{O}_2+\mathrm{H}_2\rightarrow\mathrm{H}_2\mathrm{O}+\mathrm{OH}(\Sigma)$. Accordingly, we assumed that the ignition delay time, τ_i, was approximately the time interval between two cuts, namely, the termination of the discharge and the rise of $\mathrm{OH}(\Pi)$ radicals to a certain definite value of $[\mathrm{OH}]_i$, though our recent shock-wave studies of the emission of $\mathrm{OH}(\Sigma-\Pi)$⁽¹¹⁾ ascribed the chemical excitation of $\mathrm{OH}(\Sigma)$ to the biradical reaction of $\mathrm{H}+\mathrm{O}+\mathrm{M}\rightarrow\mathrm{OH}(\Sigma)+\mathrm{M}$.

Then:

$$[\mathrm{OH}]_i = [\mathrm{OH}]_0 \exp[\{2k_1-k_4[\mathrm{M}]K_6/(K_6+k_5[\mathrm{H}_2])\}[\mathrm{O}_2]\tau_i] \quad (4)$$

Equations (1) and (4) lead to:

$$-\log(I_p) = \{2k_1-k_4[\mathrm{M}]K_6/(K_6+k_5[\mathrm{H}_2])\}[\mathrm{O}_2]\tau_i+C \quad (5)$$

provided $[\mathrm{OH}]_i$ is a certain definite value. The above relation can represent the experimental results of linear relationship between $\log(I_p)$ *vs.* τ_i.

The values of $2k_1-k_4[\mathrm{M}]\times F$ which were obtained from the slopes of the least-square lines in Figs. 2 and 3 are listed on Table 1, where F is the abbreviation of the factor $K_6/(K_6+k_5[\mathrm{H}_2])$. The difference between columns 2 and 3 on the same line of Table 1 can be expressed by: $([\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}}-[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}})k_4^{\mathrm{Ar}}\times F$, where $[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}}$ and $[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}}$ denote the third-body concentration of the two mixtures. The coefficients of the third-body ability of gas molecules on the reaction 4) had been established through experiments on the second explosion limit of hydrogen and oxygen. The coefficients of argon, helium, and oxygen, in comparison with that of hydrogen, are 0.20, 0.36 and 0.35 respectively.⁽¹²⁾ If the coefficient of argon is taken to be unity, the coefficients of helium, hydrogen, and oxygen are 1.80, 5.00, and 1.75. The superscript Ar in the above expression denotes that the coefficient for the third-body ability of argon is taken to be unity.

TABLE 1. THE VALUES FOR $2k_1-k_4[\mathrm{M}]\times F$ OBTAINED FROM THE SLOPES OF THE LEAST SQUARE LINES IN FIGS. 2 AND 3

Diluent composition %	$2k_1-k_4^{\mathrm{Ar}}[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}}\times F$ (Ar diluent) ($\mathrm{sec}^{-1}\,\mathrm{mol}^{-1}\,l$)	$2k_1-k_4^{\mathrm{Ar}}[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}}\times F$ (He diluent) ($\mathrm{sec}^{-1}\,\mathrm{mol}^{-1}\,l$)
5	1.84×10^5	2.60×10^5
15	1.86×10^5	1.47×10^5
25	1.90×10^5	1.58×10^5
35	1.91×10^5	1.63×10^5
45	2.15×10^5	1.96×10^5
55	2.51×10^5	2.30×10^5

$F=K_6/(K_6+k_5[\mathrm{H}_2])$

Reactant in the mixture is stoichiometric mixture of hydrogen and oxygen.

$[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}}$, $[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}}$: Third body concentration for reaction 4), of the mixtures with argon diluent and helium diluent. Superscript Ar denotes the third body ability of argon being stood for standard to express the third body concentration and the rate for reaction 4).

The test gas of a definite diluent composition contained a definite amount of a stoichiometric mixture of hydrogen and oxygen, and the features of the reaction may be expected to be essentially the same in both the argon-diluent and helium-diluent mixtures, and so $[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}}-[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}}$ can be attributed solely to the difference in the third-body efficiency of the diluent gases, argon and helium, or:

$$[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}}-[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}} = (1.8-1.0)[\mathrm{M}]_0 f_{\mathrm{diluent}}$$

where f_{diluent} denotes the mole fraction of the diluent gas. The ignition took place in a constant volume system, and $[\mathrm{M}]_0$ is obtainable assuming a negligible depletion of the reactant during the induction period. Thus, the values for $k_4^{\mathrm{Ar}}\times F$ were derived from a comparison of the experimental results in columns 2 and 3 in Table 1 without any further assumptions.

The values for k_1 could also be derived from the values of column 2 and/or column 3 in Table 1 and the known $k_4^{\mathrm{Ar}}\times F$ values, assuming the value for the third-body concentration $[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}}$ and/or the concentration $[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}}$, of the mixtures. In the course of the induction period the contribution of water to the reaction 4) is of no consequence, though its third-body ability is quite large.⁽¹²⁾ The contribution of other intermediate species can reasonably be ignored. The third-body concentration for the mixture with the argon diluent will then be:

$$[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{Ar}} = [\mathrm{M}]_0(f_{\mathrm{Ar}}+5.00f_{\mathrm{H}_2}+1.75f_{\mathrm{O}_2})$$

while for the mixture with the helium diluent it will be:

$$[\mathrm{M}]^{\mathrm{Ar}}_{\mathrm{He}} = [\mathrm{M}]_0(1.80f_{\mathrm{He}}+5.00f_{\mathrm{H}_2}+1.75f_{\mathrm{O}_2})$$

where f_{Ar}, f_{He}, f_{H_2}, and f_{O_2} are the mole fractions of the subscribed gases. The values for k_1 thus derived from the experimental results are listed on

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10) F. E. Belles and M. R. Lauver, *J. Chem. Phys.*, **40**, 415 (1964).

11) W. C. Gardiner, Jr., K. Morinaga, D. L. Ripley and T. Takeyama, Paper presented at the 6th International Shock Tube Symposium Freiburg Germany, April, 1967; Paper presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

12) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," 2nd Edition, Academic Press, New York and London (1961), p. 29.

TABLE 2. DERIVED VALUES OF k_1, F AND k_5/K_6 AT INDUCTION PERIOD

Diluent composition, %	k_1 ($\mathrm{sec}^{-1}\,\mathrm{mol}^{-1}\,l$)	F	k_5/K_6 ($\mathrm{mol}^{-1}\,l$)
5	—	—	—
15	6.60×10^5	1.39×10^{-2}	0.89×10^4
25	3.50×10^5	0.68×10^{-2}	2.08×10^4
35	2.41×10^5	0.42×10^{-2}	3.85×10^4
45	1.76×10^5	0.22×10^{-2}	8.70×10^4
55	1.81×10^5	0.20×10^{-2}	10.65×10^4

Table 2.

The factor F represents the fraction of atoms H which are destroyed by reacting through the reaction 4); concurrently it will show the net effect of the chain breaking in the reaction 4). The estimation of F was made by assuming the value of k_4^{Ar} in the induction period. The activation energy for the reaction 4) is a small, negative value, and the k_4^{Ar} value in the induction period can be reasonably assumed from a literature expression available elsewhere[13] if we know the approximate temperature during the induction period. An attempt was made to assume the value for k_4^{Ar} with regard to the threshold temperature. The expressions[14] for k_1 and k_4^{Ar} which were used for the estimation of the threshold temperature were $k_1=10^{11.313}\exp(-16490/\boldsymbol{R}T)$ and $k_4^{\mathrm{Ar}}=8.6\times10^8\exp(+1280/\boldsymbol{R}T)$, while the threshold expression used was $2k_1=k_4^{\mathrm{Ar}}[\mathrm{M}]^{\mathrm{Ar}}$.

The values for F thus estimated and the values for k_5/K_6 reduced from F are listed on Table 2. The values for F which appear in the table are considerably smaller than unity, signifying that the reaction 5) is predominant over the reaction 6). Miyama and Takeyama[9] have shown that the reaction 5) became significant in reproducing chain carrier radicals in low-temperature, high-pressure regime shock wave experiments. These results as well as ours possibly suggest that chain-carrier reproduction from HO_2 is predominant over the surface destruction of HO_2 under our experimental conditions.

The values for k_1 in Table 2 obtained from the experimental results resembled the literature value[14] in the temperature range between the initial temperature and the second explosion-limit temperature. Due to the small value of F, the net effect of the chain-breaking reaction 4) becomes insignificant; the accumulation of radicals might be persistent resulting in the actuation of ignition even in the temperature range where the k_1 value was observed not to be above the value of $k_4^{\mathrm{Ar}}[\mathrm{M}]^{\mathrm{Ar}}/2$. Fujimoto[15] had provided experimental evidence that in his reflected shock wave ignition, the ignition took place under the threshold temperature.

The variation in values for k_1 and k_5/K_6 in Table 2 is difficult to elucidate quantitatively because of a lack of experimental evidence about the induction-period temperature, which requires a more detailed investigation.

Summary

The induction-period reaction of silent discharge ignition in a hydrogen and oxygen system appears to be analogous to the shock-initiated reaction in a low-temperature high-pressure regime. The reaction in the discharge period may be likened to the 0th. reaction of shock-wave ignition. By comparing the argon diluent and the helium diluent systems, the net effect of chain breaking through the reaction 4) was estimated.

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[13] G. L. Schott and P. F. Bird, *J. Chem. Phys.*, **41**, 2869 (1964); R. W. Getzinger and G. L. Schott, *ibid.*, **43**, 3237 (1965); D. Gutman, E. A. Hardwidge, F. A. Dougherty and R. W. Lutz, *ibid.*, **47**, 4400 (1967).

[14] W. C. Gardiner, Jr., K. Morinaga, D. L. Ripley and T. Takeyama, *ibid.* **48**, 1665 (1968).

[15] S. Fujimoto, This Bulletin, **36**, 1233 (1963).