BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1368—1372 (1967)

Effect of Electric Fields on Gamma Radiolysis of Methanol Vapor

Tadayuki OHMAE and Hiroshi SAKURAI

The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka

(Received December 20, 1966)

Electric fields were applied during the irradiation of methanol vapor up to voltages necessary to cause secondary ionization. The yields per ion pair of 3.00±0.02, 0.39±0.02, and 0.120±0.003 were estimated for hydrogen, carbon monoxide, and methane respectively by relating the product yields to the saturation ion current measured during the irradiation. The hydrogen yields decreased in the saturation current region, while the carbon monoxide and the methane yields remained nearly constant. The reduction of hydrogen yield may be ascribed to a suppression of dissociative electron-capture process $CH_3OH + e \rightarrow CH_3O^- + H$ by a fast electron-absorption to the anode. The contribution of molecular or hot hydrogen atom process to the formation of hydrogen was found to increase with an increase of the electric field strength.

Applications of electrostatic fields in the vapor phase radiolysis have attracted much interest in recent years and considerable efforts have been channeled toward determination of the degree and mode of decompositions through ion-molecule reactions or neutral excited molecules formed by electron impact. The great majority of work, however, has dealt almost exclusively with hydrocarbons[1-8] and little attention has been paid to highly polar compounds.[9]

In the present investigation, methanol vapor was chosen as a polar compound and irradiated under the application of electric fileds, because extensive studies had been made on the mechanism of its γ-radiolysis.[10-12] The effect of added propylene was also studied to obtain a quantitative estimate of the number of hydrogen molecules produced through molecular or hot atom process in both the saturation current region and the electron multiplication region.

Experimental

Materials. Extra-pure methanol (Wako Pure Chem. Indust. Co.) was fractionated after refluxing with dinitrophenylhydrazine and sulfuric acid for about 12 hr to remove ketonic impurities. The middle fraction was refluxed over clean magnesium tunnings and distilled. The middle third of the distillate was subjected to trap to trap distillations just before each use. Propylene (Takachiho Chem. Indust. Co., 99.5%) was used without further purification.

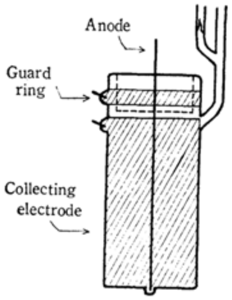

Fig. 1. Irradiation vessel.

Irradiations. The irradiation vessel is illustrated in Fig. 1. It was virtually the same type as that had been used by Back *et al.*[1] and the effective part was 530 *ml* volume. It was made of soft-glass tubing approximately 21 cm in height and 6 cm in diameter. It was thoroughly baked out under vacuum for about 5 hr before each sampling.

Irradiations were done with 5000 curies ^{60}Co source at room temperature. The average dose rate across the irradiation vessel was about $5.5 \times 10^{17}\ eV \cdot g^{-1} \cdot min^{-1}$. The maximum dose corresponded to a methanol decomposition of approximately 0.5%; $7.9 \times 10^{20}\ eV \cdot g^{-1}$. The application of electric fields and the measurement of saturation ion current were carried out according to the method described by Back *et al.*[1]

Analyses. Gaseous products not condensed by liquid nitrogen were transfered to a gas burette for a

---

[1] R. A. Back, T. W. Woodward and K. A. McLauchlan, *Can. J. Chem.*, **40**, 1380 (1962).

[2] T. W. Woodward and R. A. Back, *ibid.*, **41**, 1463 (1963).

[3] H. Essex, *J. Phys. Chem.*, **58**, 42 (1954).

[4] G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1963).

[5] P. Ausloos and R. Gorden, Jr., *ibid.*, **41**, 1278 (1964).

[6] G. G. Meisels and T. J. Sworski, *J. Phys. Chem.*, **69**, 2867 (1965).

[7] H. H. Carmichael, R. Gorden, Jr., and P. Ausloos, *J. Chem. Phys.*, **42**, 343 (1965).

[8] R. D. Doepker and P. Ausloos, *ibid.*, **44**, 1951 (1966).

[9] S. Takamuku and H. Sakurai, This Bulletin, **38**, 791 (1965).

[10] J. H. Baxendale and R. D. Sedgwick, *Trans. Faraday Soc.*, **57**, 2157 (1961).

[11] G. M. Meaburn and F. W. Mellow, *ibid.*, **61**, 1701 (1965).

[12] G. M. Meaburn, F. W. Mellow and A. Reiffsteck, *Nature*, **204**, 1301 (1964).

measurement of the total volume by a Teopler pump and then hydrogen was analyzed by passage through a palladium thimble heated up to 300°C. The individual components, carbon monoxide and methane, were determined by gas-solid chromatography. Complete separation was accomplished with a 3 m column of activated charcoal at 70°C. Hydrogen was used as carrier gas at the flow rate of 50 ml·min^{-1}.

Results

Ion Current Curve. Figure 2 shows the dependence of ion current on applied voltage for five different gas pressures. The shape of these current curves are essentially almost identical with each other when they are drawn against the ratio of electric field X to pressure P. In contrast with the cases reported about hydrocarbons, the saturation ion current increased gradually with increasing field strength and therefore the saturation current plateaus were not perfectly flat. Moreover, the range of electric field stregnth corresponding to the saturation region was fairly narrow and a rapid increase of ion current set in at such a low field strength as 10 V·cm^{-1}·mmHg^{-1}. These characteristics of ion current curve could be related to the large electron-affinity of methanol vapour as well as the increase of numbers of small fragment cations caused by the impact of accelerated electrons.

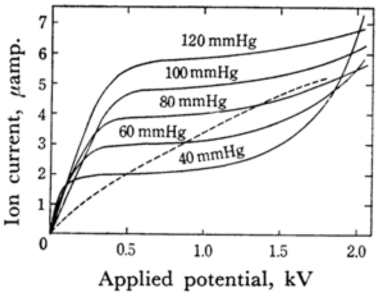

Fig. 2. Ion currents in the γ-radiolysis of methanol at various pressures.
---- Ion current observed when electric field was applied reversely at 80 mmHg.

When the electric field was applied with the central electrode negative so that the positive ions were drawn to this electrode and electrons to the other, the saturation current plateau was not observed and the ion current increased almost linearly as shown by a broken line in Fig. 2. This suggests that the positive ions diffuse to the electrode much slower than the electrons.

The range of the field strength and the ion current corresponding to the saturation current region changed quite linearly with gas pressure as shown in Fig. 3. From the slope of the line, the number of ion pairs produced in 1 mmHg of gas per unit time was calculated to be (3.04±0.02) × 10μ mmHg^{-1}·sec^{-1}.

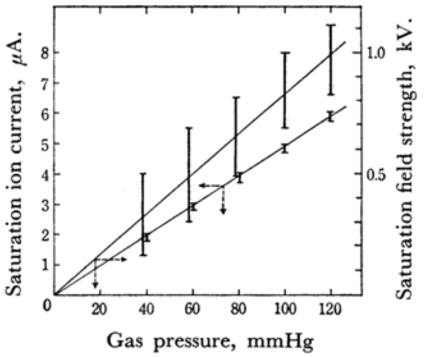

Fig. 3. Saturation ion current and field strength as a function of methanol pressure.

Absolute Product Yields. Figure 4 shows the dependence of the product yield on the gas pressure in the absence of the electric field. Each was linear with gas pressure and the values of the yield per ion pair, M/N_s, were obtained from the slopes and the saturation ion current, *i. e.*, 3.00± 0.02 for hydrogen, 0.39±0.02 for carbon monoxide, and 0.120±0.003 for methane.

Baxendale and Sedgwick[10] gave 27.7 eV for W-value, the average energy absorbed per ion pair, in their study of correlating the product distribution with the mass spectral pattern of methanol. Taking this W-value, G-values of the various products were calculated as shown in Table 1. The values obtained by Baxendale *et al.*[10] and Meaburn *et al.*[11] were also included for comparison. Nitrous oxide was used as a dosimetry assuming $G(N_2)=9.68$ in their studies. The good agreement of data for hydrogen and methane was seen between the present work and the reference (11). In addition to the linear

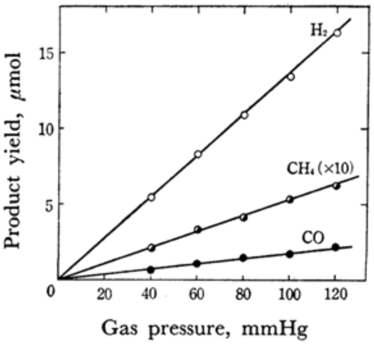

Fig. 4. Product yields of radiolysis for 24 hr as a function of methanol pressure.

Table 1. G-Values of gaseous products

Product	Present work	Ref. 10	Ref. 11
$G(H_2)$	10.84±0.07	10.4	11.1 ±0.6
$G(CO)$	1.41±0.07	0.84	1.18±0.05
$G(CH_4)$	0.42±0.01	0.26	0.35±0.06

TABLE 2. SOME KINETIC PARAMETERS OF THE HYDROGEN FORMATION REACTIONS

X/P	$G(H_2)_{total}$	$G(H)_s$	$G(H_2)_{mol}$	k_4/k_3
0	10.84±0.07	8.48±0.15	2.36±0.05	2700±100
3.2	9.77±0.07	6.41±0.10	3.36±0.10	2700±100
6.8	17.33±0.07	11.90±0.10	5.43±0.10	1500±100
0*1	11.1 ±0.6	9.0 ±0.6	2.1 ±0.1	3000±700

*1 The results obtained by Meaburn and Mellows.11)

dependences of the product yield with gas pressure, the fair agreement suggests that the absorption of gaseous products by the electrode coated with graphite is entirely negligible and that the *W*-value used by them is quite reasonable.

Effect of Electric Field. The effect of electric field on the yields of hydrogen, carbon monoxide and methane from the radiolysis at 100 mmHg pressure is shown in Fig. 5. The hydrogen yield decreased in the saturation region to the extent of 88% of the original yield, while the carbon monoxide and the methane yield remained almost unchanged.

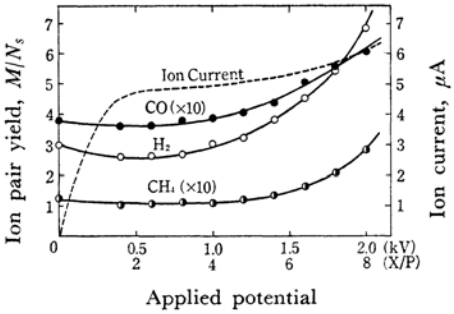

Fig. 5. The effect of electric field on the product yields from the γ-radiolysis of methanol. Methanol pressure, 100 mmHg

The fairly sharp increase of the hydrogen yield set in just before the onset of electron multiplication. The carbon monoxide and the methane yield increased more slowly than hydrogen yield in the electron multiplication region.

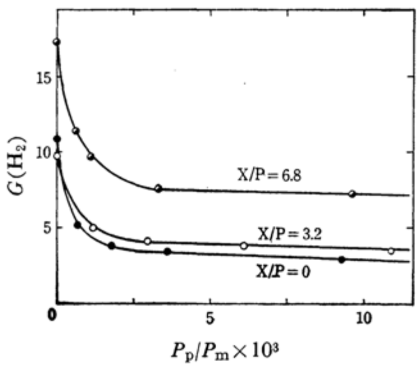

Fig. 6. The effect of added propylene on the hydrogen yield at three different electric field strength.
Methanol pressure, 100 mmHg

Effect of Added Propylene. To obtain an information about the contribution of molecular or hot atom process to the various product formation, propylene was added as a scavenger at three different electric fields; $X/P=0$ (no field), $X/P=3.2$ (the saturation region), and $X/P=6.8$ (the electron multipleication region). The hydrogen yield, which was represented as the $G(H_2)$ value to allow comparison to be made with the results of Meaburn and Mellows,11) decreased rapidly upon increasing the propylene concentration in all regions as shown in Fig. 6. Both the carbon monoxide and the methane yield, however, were kept nearly constant in either of three regions.

Discussion

Baxendale and Sedgwick10) accounted quantitatively for all the product yields with the mass spectral pattern of methanol. They assumed the rapid initial ion-molecule reactions of CH_3OH^+, CH_2OH^+, and CHO^+ with methanol to form the cation $CH_3OH_2^+$ and the only subsequent neutralization reaction (1).

$$CH_3OH_2^+ + e^- \rightarrow CH_3OH + H \qquad (1)$$

The dissociative electron-capture process (2) could be added as a mode of the electron fate.

$$CH_3OH + e^- \rightarrow CH_3O^- + H \qquad (2)$$

The same decay process of electron was also suggested in the radiolysis of liquid methanol13) as well as solid methanol at −196°C.14) The analogous electron attachment reactions of methanol by aromatic anions, arene⁻, to form the anion CH_3O^- were confirmed in the pulse radiolysis of liquid methanol15);

$$\text{arene}^- + CH_3OH \rightarrow \text{arene-H}\cdot + CH_3O^-.$$

The study of negative ion mass spectra by Melton and Rudolph16) showed that the anion

---

13) J. H. Baxendale and F. W. Mellow, *J. Am. Chem., Soc.*, **83**, 4720 (1961).

14) F. S. Dainton, G. A. Salmon and J. Teply, *Proc. Roy. Soc. (London)*, **A286**, 27 (1965).

15) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

16) C. E. Melton and P. S. Rudolph, *ibid.*, **31**, 1485 (1959).

CH_3O^- is indeed one of the main abundant anions.

Therefore, electrons as well as hydrogen atoms should be considered as the probable precursors of scavengeable hydrogens. The rapid decrease of the hydrogen yield by the addition of propylene could be attributed to the following competition between methanol and propylene for hydrogen atoms.

$$H + CH_3OH \xrightarrow{k_3} H_2 + CH_2OH \qquad (3)$$

$$H + C_3H_6 \xrightarrow{k_4} C_3H_7 \qquad (4)$$

The following relationship should be held in this system;

$$\frac{1}{\varDelta G(H_2)} = \frac{1}{G(H)_s}\left\{1 + \frac{k_3P_m}{k_4P_p}\right\}$$

where $\varDelta G(H_2)$ is the observed decrease in hydrogen yield, $G(H)_s$ is the yield of the scavengeable hydrogen (G_H+G_e), and P_m and P_p are the partial pressures of methanol and propylene, respectively.

The plots of $1/\varDelta G(H_2)$ against P_m/P_p are shown in Fig. 7. The equation holds reasonably well in all of the three different regions. The values of k_4/k_3, $G(H)_s$ and $G(H_2)_{mol}$ are obtained from the three straight lines as summarized in Table 2. $G(H_2)_{mol}$ means the G-value of hydrogen produced through molecular or hot hydrogen atom process. The agreement with the results obtained by Meaburn and Mellows[11] in no field region is fairly satisfactory.

The charge transfer reaction (5) from parent cation CH_3OH^+ to propylene was reported[12] to be exothermic to the extent of 1.1 eV.

$$CH_3OH^+ + C_3H_6 \rightarrow CH_3OH + C_3H_6^+ \qquad (5)$$

However, the degree of this reaction will be negligible, because the concentration of added propylene was less than 1% in the present work and therefore the rapid proton transfer reaction (6) will be much favourable.

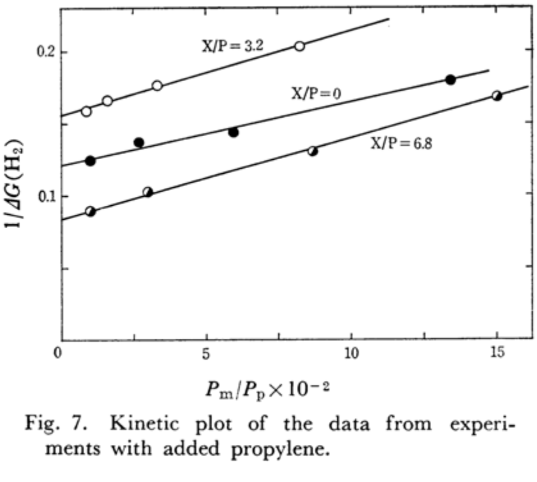

Fig. 7. Kinetic plot of the data from experiments with added propylene.

$$CH_3OH^+ + CH_3OH \rightarrow CH_3OH_2^+ + CH_2OH \qquad (6)$$

Figure 8 shows the dependences of $G(H_2)_{total}$, $G(H)_s$, and $G(H_2)_{mol}$ on the strength of applied electric field. The yield of molecular hydrogen, $G(H_2)_{mol}$, increased almost linearly with increasing field strength, while the yield of scavengeable hydrogen reached bottom in the saturation region and increased rapidly in the electron multiplication region.

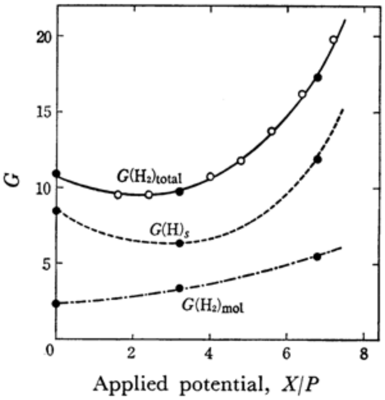

Fig. 8. The effect of applied electric fields on the hydrogen formation processes.

Meisels and Sworski[7] suggested that the primary ionizations and the initial ion-molecule reactions should not be altered by the application of electric fields during irradiation. They also suggested on the effect of electric fields that the rapid heterogeneous neutralization at or near the electrode take the place of the homogeneous ion recombination in the gas phase and the frequency of charge-molecule interactions are reduced by the influence of the increased energy on the cross section for such process.

According to their suggestion, the neutralization reaction (1) and the dissociative electron-capture (2) will be the main processes on which the applied electric field influences. It could be assumed that one hydrogen atom is produced even if the heterogeneous neutralization of the acid species $CH_3OH_2^+$ undergoes at the electrode instead of the homogeneous neutralization in gas phase. On the other hand, the process (2) will be greatly suppressed by the fast collection of electrons to the anode. If the above assumption is allowed, the observed reduction of the scavengeable hydrogen yield in the saturation region, about 20% of the total hydrogen yield in no field region, may correspond to this suppression of the process (2).

In the electron multiplication region, the following secondary ionizations caused by the accelerated electron would take place on the analogy of mass spectral pattern.

$$CH_3OH + e^* \rightarrow CH_3OH^+ + 2e \quad (7)$$

$$CH_3OH + e^* \rightarrow CH_2OH^+ + H + 2e \quad (8)$$

$$CH_3OH + e^* \rightarrow CHO^+ + H_2 + H + 2e \quad (9)$$

The rapid enhancement of scavengeable hydrogen in the region of high field strength ($X/P>4$) could be reasonably ascribed to those secondary ionizations. The large drop of the ratio k_4/k_3 in this region suggests that the hydrogen atoms produced by the above accelerated-electron impact have fairly higher energy and undergo the hydrogen abstraction from methanol (3) much rapidly as compared with those in the lower field strength.

The yield of molecular hydrogen increased even in the saturation region. This suggests that the following excitation of methanol by accelerated electrons should be involved as a significant process in addition to the initial direct excitation.

$$CH_3OH + e^* \rightarrow CH_3OH^* + e \quad (10)$$

$$CH_3OH^* \rightarrow CH_2O + H_2 \quad (11)$$

It was proposed by Baxendale and Sedgwick[10] from the mass spectral data that carbon monoxide and methane are produced entirely by the hydride-ion transfer reaction (12), the proton transfer reaction (13), and the charge transfer reaction (14).

$$CH_3^+ + CH_3OH \rightarrow CH_4 + CH_2OH^+ \quad (12)$$

$$CHO^+ + CH_3OH \rightarrow CO + CH_3OH_2^+ \quad (13)$$

$$CO^+ + CH_3OH \rightarrow CO + CH_3OH^+ \quad (14)$$

These ion-molecule reactions undergo quite rapidly before neutralization by electrons. These mechanisms would be supported by the fact that the yields of carbon monoxide and methane were not affected in the saturation current region. The failure of propylene to reduce either of two products is also consistent with these mechanisms.