

ノート

赤外による $\text{CH}_3\text{OH}-\text{T}_2\text{O}$ 系の分解過程の研究

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Infrared Study of Decomposition Process in $\text{CH}_3\text{OH}-\text{T}_2\text{O}$ System.

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Abstract

The decomposition process in the $\text{MeOH}-\text{T}_2\text{O}$ system was studied over a period of 10 months by infrared spectroscopy. The main product was CO with a small amount of CH_4 and HCO_2Me . The process was kinetically analyzed, which clarifying that the decomposition of MeOH and CO almost obeys first- and second-order kinetics, respectively. The G value derived for decomposition was -3.5 for MeOH and -11 for CO. These values are different from those received from radiolysis. The reason for this will be discussed.

γ -Radiolysis of gaseous methanol has been studied extensively by using ^{60}Co as a source [1 - 7]. The main product is H_2CO and ethylene glycol. On the other hand, we have found quite a different result from the present system [8] (the main product being

CO), observing infrared spectra over a period of 10 months. The difference in both radiolyses has been discussed on the basis of surface reactions on stainless steel masking the formation of H_2CO and ethylene glycol while CO is enhanced, when stainless steel is used as an infrared cell.

The difference in abundance is one of characteristics in the present system, especially in the initial stage. When further decomposition takes place, it is expected that the decomposition process may be complex due to change in species or components formed. In fact, some secondary reactions were found. In the present study we will report the kinetics over a period of 10 months and derive G values.

T_2O used was prepared from oxidation of T_2 by CuO at 350°C . The amount was estimated to be 0.70 Ci from the pressure. The initial molar ratio of $\text{MeOH}/\text{T}_2\text{O}$ was 16, where initial pressure of methanol was 40 torr in the infrared gas cell. The cell was made of stainless steel with KRS-5 plates as windows [9] and kept at 50°C . The infrared spectrum was observed using a JASCO-IRA-302 spectrometer in the region of $4000\text{--}330\text{ cm}^{-1}$.

HCO_2Me was obtained commercially. CO was prepared from dehydration of HCO_2H by H_2SO_4 , removing O_2 by basic pyrogallol. CH_4 was got from a reaction of MeMgI with H_2O . Their infrared spectra were observed for obtaining calibration curves; the bands used are: 2143 cm^{-1} for CO, 1306 cm^{-1} for CH_4 and 1756 cm^{-1} for HCO_2Me , and 3672 cm^{-1} for MeOH . The time course of MeOH , CO, CH_4 and HCO_2Me is given by torr in Fig. 1, where t is a time by day; T_2O or HTO was not observed clearly [8].

The decomposition rate of MeOH is, as a whole, slow in Fig. 1, taking ~ 5 months for decomposing half of methanol. This depends, of course, on the amount of tritiated water used. Decomposition takes place through ionization or excitation by β -rays. This suggests two simple cases for the process: (i) the zeroth- or (ii) the first-order kinetics. The case (i) or (ii) is expected when whole energy of β -rays is used or not for decomposition, respectively. The observed time course is not linear in Fig. 1, though it is somewhat obscure due to errors in mea-

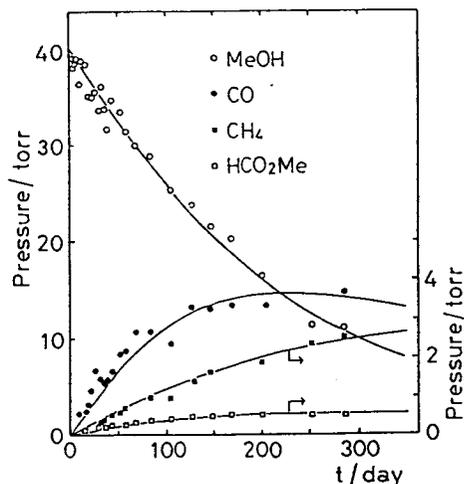


Fig. 1. Change in pressure of some species with t in $\text{MeOH-T}_2\text{O}$ system. Solid lines indicate fitted ones.

surement. It seems that the time course differs somewhat from the first-order kinetics, since it depends slightly on time. That is, the process should be accelerated with t . This suggests energy transfer from excited states of species formed, eg., CO⁺ or CH₄⁺, to MeOH, resulting in acceleration of decomposition. This model was assumed as follows :

$$-\frac{d[\text{MeOH}]}{dt} = k_1 [\text{MeOH}] \{ 1 + \alpha_0 ([\text{CO}] + [\text{CH}_4]) \} [\text{T}] \quad (1)$$

where the term on α_0 represents a contribution of energy transfer, and k_1 is the rate constant, brackets concentration by torr and T given by:

$$[\text{T}] = [\text{T}_0] \exp(-t/6460), \quad (2)$$

where $[\text{T}_0]$ is the initial pressure, 5.0 torr, and $1/6460 \text{ day}^{-1}$ the time constant of β -decay; it was assumed that a decomposition process depends linearly on $[\text{T}]$, whereas $[\text{T}]$ was regarded as zeroth-order in kinetics.

In Fig. 1 we have a relation that MeOH decomposed is nearly same in amount as CO formed at $t < 100$, though it does not hold on at $t > 100$. This is quite different from results in γ -radiolysis [1 - 7], where CO is formed slightly, as described above. The formation of CO is steep at $t < 100$, following to gentle in Fig. 1. This indicates clearly a secondary reaction in a comparable rate with decomposition of MeOH. The process was not fitted by use of the first-order kinetics. Thus, we examined the process as follows :

$$\frac{d[\text{CO}]}{dt} = -k_2' \frac{d[\text{MeOH}]}{dt} - k_3 [\text{CO}]^n [\text{T}] \quad (3)$$

where $n > 1$ and k_2' is defined using a real rate constants k_2 as $k_2 = k_2' \times k_1$; k_i' is, hereafter, defined similarly. It should be noted that the detail for the second term is unknown in a sense that species from the process have not been confirmed; condensed matters may be formed mainly.

CH₄ is formed almost linearly with t , whereas HCO₂Me behaves similarly to CO in Fig. 1. These were also fitted by use of the expressions :

$$\frac{d[\text{CH}_4]}{dt} = -k_4' \frac{d[\text{MeOH}]}{dt} - k_5 [\text{CH}_4] [\text{T}] \quad (4)$$

and

$$\frac{d[\text{HCO}_2\text{Me}]}{dt} = -(1 - k_2' - k_4') \frac{d[\text{MeOH}]}{dt} - k_6 [\text{HCO}_2\text{Me}] [\text{T}] \quad (5)$$

Another species, Me₂O and CH₂(OMe)₂, were omitted from the analysis because of

small amounts. The results are given by solid lines in Fig. 1, where the parameters used are: $k_1=0.78$, $k_2=0.69$, $k_4=0.066$, $k_5=0.018$ and $k_6=0.60 \times 10^{-3}$ in $\text{torr}^{-1} \text{ day}^{-1}$, $k_3=0.60 \times 10^{-4}$ in $\text{torr}^{-2} \text{ day}^{-1}$, and $\alpha_0=0.017 \text{ torr}^{-1}$ and $n=2.0$.

The fit between the observed and calculated results is well, which may indicate adequacy of the present analysis. That the value due to $\alpha_0\{[\text{CO}]+[\text{CH}_4]\}$ is < 0.25 , especially at $t < 100$ in Eq. (1), shows that the process is almost first-order. A reaction of CO with H_2 may be found as the second-order kinetics, because the amount of $[\text{H}_2]$ is almost twice of $[\text{CO}]$. The fact of $n=2$ in Eq. (3) suggests this reaction rather than a reaction of CO itself; paraformaldehyde may be formed dominantly, though formation of CO_2 , H_2O and so on [10–13] is also expected. The fact of $k_5 \approx 0$ indicates that CH_4 is also a secondary product. This is expected reasonably from decomposition of HCO_2Me and also from a reaction of $\text{CO}+\text{H}_2$ [13–15].

The G values of species X may be derived as [16]:

$$G = \frac{d[\text{X}]}{57 d[\text{T}]_\beta} = \frac{d[\text{X}]}{dt} \bigg/ \frac{d[\text{T}]_\beta}{dt} 57 = \frac{v_x}{57 v_\beta} \quad (6)$$

where a factor 57 originates in energy of β -rays (5.7 keV in average). In Eqs. (3)–(5) v_x consists of two terms. The first term is important at $t \approx 0$ and gives G values for formation. They are given in Table 1. On the other hand the second term depends largely on t , namely, pressure. Thus, we estimated the G value for decomposition at the normalized pressure in 40 torr, using the rate constant in the second term in Eqs. (3), (4) and (5). They are also given in Table 1.

Table 1. G values for decomposition ($-G$) and formation (G) in MeOH- T_2O system.

	MeOH	CO	CH_4	HCO_2Me
G	—	3.1	0.30	0.11
$-G^*$	3.5	11	0.08	2.7

*Normalized values in 40 torr.

The G value of MeOH, -3.5 , is considerably small rather than that, -11 , in γ -radiolysis [1–7]. One of reasons is clear from Eq. (1), which means that the G value depends on pressure. The others may be reproduction of MeOH by surface reactions, as has been pointed out [8]. These suggest that a considerable amount of energy of β -rays, $\sim 50\%$ even at $t \approx 0$, is lost at a wall of the cell. The $G(-\text{CO})$ value of ~ 8 has been obtained from electron impact in CO and $\text{CO}-\text{H}_2$ systems [10–

13]. The result obtained here is, thus, quite large, by referring also to the energy loss, described above. Although the reason is obscure, reactions of CO with stainless steel may take place to some extent. The $G(-CH_4)$ value, 0.08, indicates clearly that the decomposition reaction is comparable with secondary reactions for formation, as described above.

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