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## METHANE AND n-BUTANE OXIDATION WITH CO<sub>2</sub> UNDER RADIOFREQUENCY PLASMAS OF MODERATE PRESSURES (\*)

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**Résumé.** — L'oxydation du méthane et du n-butane avec CO<sub>2</sub> a été étudiée dans des décharges électriques de 35 MHz sous une pression de 20 torr en variant, vitesses de flux (6-30 l (TPS) min.<sup>-1</sup>), et puissance spécifiques (2-8 cal cm<sup>-3</sup> s<sup>-1</sup>). Les résultats présentés mettent en évidence la première étape du processus, qui est la rupture d'une liaison C-H, puis une seconde, l'oxydation des hydrocarbures intermédiaires en C<sub>2</sub> (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) qui est la voie principale pour convertir méthane et n-butane en CO.

**Abstract.** — The oxidation of methane and n-butane with CO<sub>2</sub> has been studied in 35 MHz electrical discharges, operated at variable gas flow rates (6-30 l (STP) min<sup>-1</sup>), power densities (2-8 cal cm<sup>-3</sup> s<sup>-1</sup>) and constant pressure of 20 torr. Evidence is presented that the primary step of the process is the rupture of a C-H bond and that the main route for the conversion of both methane and n-butane into CO is via the intermediate C<sub>2</sub>-hydrocarbons (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>).

**1. Introduction.** — Radiofrequency discharges operated at moderate pressures (5-50 torr) have recently been used for detailed investigations of H<sub>2</sub> [1], CO<sub>2</sub> dissociation [2] and for C<sub>1</sub>-C<sub>4</sub> hydrocarbons cracking [3]. In these studies, evidence has been presented for the existence of a mechanism of molecular dissociation involving vibro-rotationally excited molecules, the population of which is maintained by the electric field at levels substantially higher than those corresponding to the kinetic gas temperature. Spectroscopic investigations [4a, b], carried out under similar discharge conditions, have confirmed the existence of remarkable disequilibrium among the various degrees of freedom.

Similar conclusions are theoretically supported by a model of molecular dissociation for systems characterized by strong disequilibrium, recently developed by Capitelli *et al.*, which has been successfully applied to H<sub>2</sub> [5] and N<sub>2</sub> [6] dissociation.

The results obtained for the oxidation of methane and n-butane with CO<sub>2</sub>, under discharge conditions very similar to those previously used, will be reported in this note.

**2. Experiment.** — The discharge reactor is a vertical tube of quartz 3.5 cm i. d., 1 m long, surrounded by a refrigerating water jacket, which is also used for calorimetric measurements of the power dissipated from the gas to the reactor walls. It is capacitively coupled to the radiofrequency generator (35 MHz, 10 kW of STEL, Massy, France) by means of two external annular electrodes of copper, 3.5 cm high, set at a fixed separation of 18 cm, including the electrode height.

The process has been studied by feeding the reactor with 1 : 1 mixtures of methane and carbon dioxide and with 1 : 1, 1 : 4 mixtures of n-butane and CO<sub>2</sub>, at variable total flow rates ( $\dot{V}_T = 6 - 34$  l(STP) min<sup>-1</sup>) and power densities ( $\langle W \rangle = 2-8$  cal cm<sup>-3</sup> s<sup>-1</sup>) and constant pressure of 20 torr. Experimental details on discharges parameters, sampling procedure, gas analysis and mass balance of the reacted gas can be found in ref. [1-2].

In particular, the reacted gas collected in carefully calibrated glass bulbs, was quantitatively analyzed by means of a gas chromatograph. Stainless steel columns, 2 mm i. d. and 9 m long, filled in part with Porapak Q and in part with Porapak T, working with programmed temperature rise from - 60 °C to 120 °C, have been found to give a good separation of all reaction products, which for both methane and n-butane, are hydrogen,

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carbon dioxide, acetylene and small amounts of ethylene and ethane. Water, if present, is within the detection limits of the gas chromatograph.

By means of appropriate mass balance equations, one can evaluate the degree of conversion  $\beta$  of methane and/or n-butane into CO and into C<sub>2</sub>-hydrocarbons (i. e. acetylene, ethylene, ethane) and the total degree of conversion  $\beta_T$ . Since water and oxygen have not been detected in appreciable amounts, the degree of conversion of CO<sub>2</sub> into CO ( $\beta_{CO_2}^{CO}$ ) is practically coincident with that of methane into CO ( $\beta_{CO}^{CH_4}$ ), while for n-butane one has

$$\beta_{CO}^{CO_2} = 4 R \beta_{CO}^{C_4H_{10}}$$

where  $R$  is the ratio between n-butane and carbon dioxide in the gas mixture.

In figure 1 we have plotted the total conversion, together with the conversion into CO and C<sub>2</sub>-hydro-

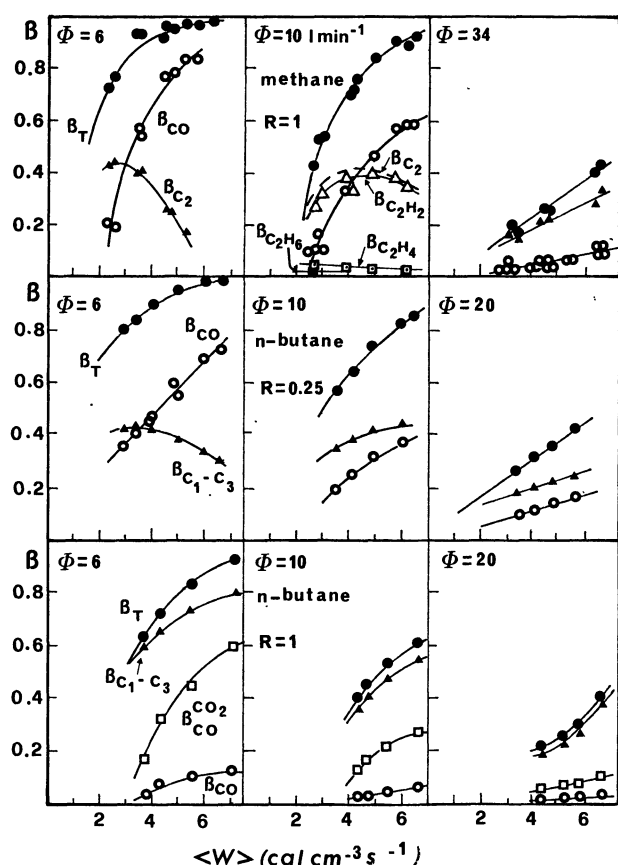


FIG. 1. Degrees of conversion (total  $\beta_T$ , into CO,  $\beta_{CO}$ , and into C<sub>2</sub>-hydrocarbons,  $\beta_{C_2}$ ) of methane and n-butane, as a function of the power density for three values of total gas flow rates.

carbons, for the three mixtures studied, as a function of the power density at three values of total flow rate. We have also reported in this figure, for one methane flow rate, the observed conversion in each C<sub>2</sub>-hydrocarbon, which indicate that acetylene is the main C<sub>2</sub>-hydrocarbon. Similar distribution of C<sub>2</sub>-hydrocarbons have been found for other conditions.

A kinetic analysis of these data requires the evaluation of the residence time, a function of the initial flow rate, the mean temperature within the reaction zone and the volume variations due to the decomposition processes.

The problem of gas temperature measurements under this type of discharge has been discussed in ref. [1, 2, 7, 8]. Since the discharge conditions are very similar to those used in ref. [1, 2, 3], where values of  $T_g$  have been estimated on the basis of energy balance equations, an estimated average temperature  $T_g = 800 \pm 150$  K has been assumed for all experimental conditions. The volume changes have been evaluated on the basis of the extent of conversion into stable products, neglecting volume changes due to free radicals.

With these assumptions, mean residence times have been evaluated and the plots of figure 2 obtained.

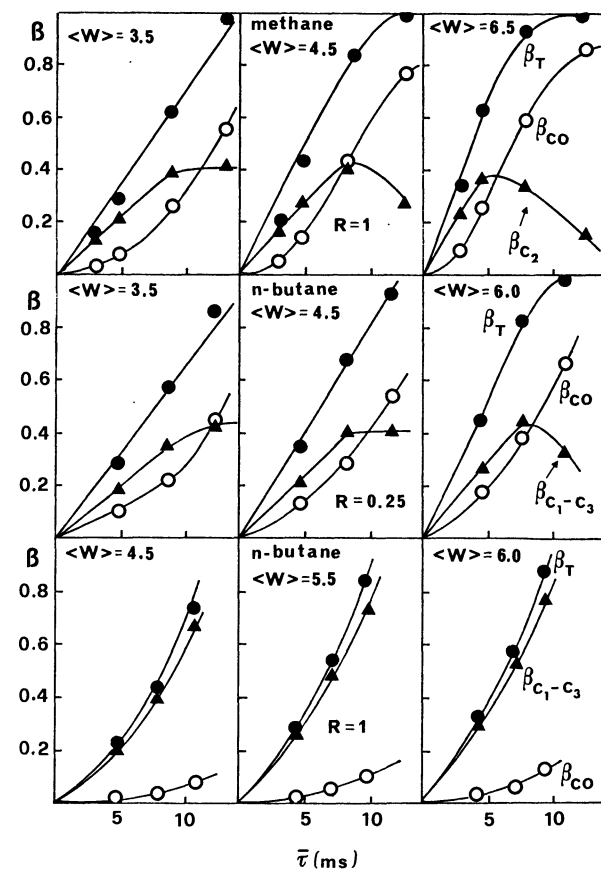


FIG. 2. — Degrees of conversion of methane and n-butane as a function of the mean residence time for three values of power density.

**3. Discussion.** — The results of figure 2 show that the total conversion of both methane and n-butane follows closely an apparent zero order kinetic law, up to 80-90 % conversion. The process is slightly self accelerated for n-butane/CO<sub>2</sub> mixtures with  $R = 1$ .

The behaviour illustrated by figure 2, with a maximum in the  $\beta_{C_2}/\bar{\tau}$  curves, and with the definite acceleration indicated by the  $\beta_{CO}/\bar{\tau}$  plots, is typical of processes

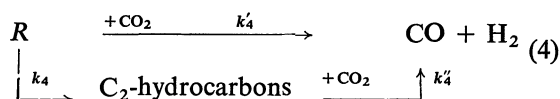
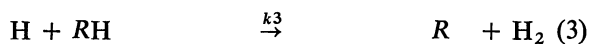
in which the conversion into final products is via intermediate species :  $A \rightarrow B \rightarrow C$ .

Similarities with the previously studied behaviour of C<sub>1</sub>-C<sub>4</sub> decomposition [3] should also be stressed :

- i) the kinetics are close to zero order for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and slightly self accelerated for n-butane ;
- ii) rates are of the same order of magnitude (see also below) ;
- iii) the distribution of C<sub>2</sub>-hydrocarbons is similar to that of figure 1.

These observations suggest that the rate determining step of the process should be the same as that observed in the decomposition of the same hydrocarbons in mixture with hydrogen, and that the main route for the conversion of both methane and n-butane into CO and H<sub>2</sub> is via the intermediate C<sub>2</sub>-hydrocarbons.

A reaction scheme which could account for the above observations, is the following :



Reactions (1-3) are those utilized and discussed for a description of the kinetics of C<sub>1</sub>-C<sub>4</sub> cracking. In that case reactions (1-3) are followed by the conversion of the radical R into C<sub>2</sub>-hydrocarbons and, eventually, into acetylene ; in the presence of CO<sub>2</sub>, they are followed by reactions (4). Losses of H-atoms by heterogeneous and homogeneous recombinations can definitely be neglected in the presence of hydrocarbons as  $k_3$  is very high [9, 10]. Estimation of processes, like  $R + H \rightarrow RH$ ,  $R + H_2 \rightarrow RH + H$ , etc., is very uncertain particularly under discharge conditions ; these contribution have not been included,

According to this simplified scheme, and assuming a stationary state for H-atoms, one gets the following expression for the hydrocarbon conversion rate

$$-d|RH|/dt = 2k_1|RH| + 2k_2|H_2|. \quad (5)$$

Since the concentration of hydrocarbon decreases, while that of hydrogen increases with time, both a zero order kinetics and the self accelerated process observed for n-butane can result from equation (5), for appropriate values of the rate constants, i. e.  $k_1 \approx k_2$ . Further details on this point have been discussed in the paper on the decomposition of C<sub>1</sub>-C<sub>4</sub> hydrocarbons.

Equation (5) can be expressed in terms of the total degree of conversion  $\beta_T$ , by the following integrated expression :

$$\frac{1}{(i-1)} = \ln [1 + (i-1)\beta_T] = 2k_1\bar{\tau} \quad (6)$$

where

$$i = \frac{(n+2)\beta_T + n\beta_{CO}}{2\beta_T}$$

with  $n$  = number of C-atoms of the hydrocarbon. This requires  $i$  to be independent of  $\beta_T$ . Values of  $i$  have been found to be approximately constant up to 80-90 % conversion and equal to  $1.66 \pm 0.1$  for methane and  $3.80 \pm 0.1$  for n-butane.

Equation (6) fits the experimental data, as shown in figure 3. From the slopes of these plots, values of  $k_1$

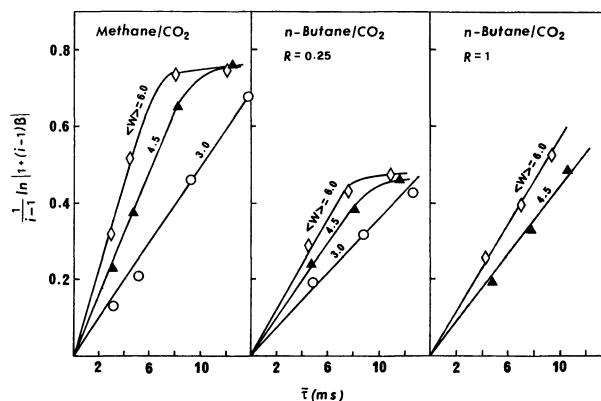


FIG. 3. — Conversion data of methane and n-butane plotted according to equation (6) for three values of power density.

have been derived at different power densities and collected in figure 4. These values do not differ by more than a factor of 2 from those derived from the kinetics of the corresponding hydrocarbon in mixture with

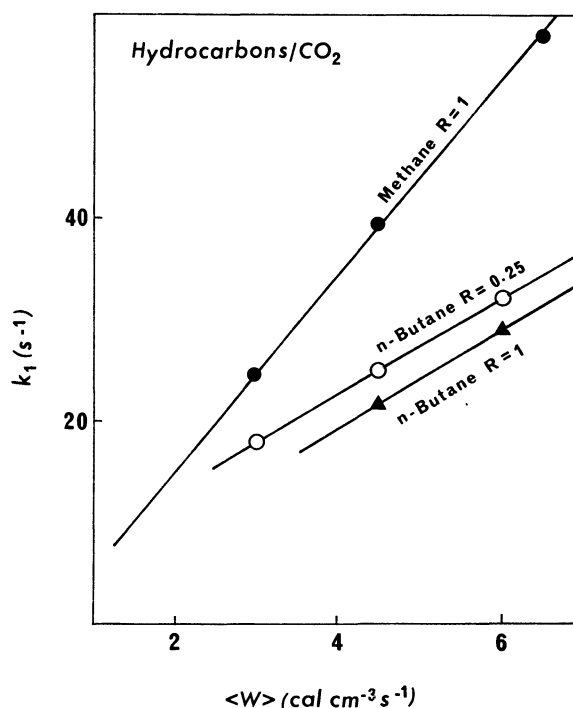


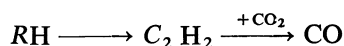
FIG. 4. — Values of  $k_1$  as a function of the power density.

hydrogen [3]. These results show that  $\text{CH}_4$  and  $\text{C}_4\text{H}_{10}$  disappear with the same kinetics and at comparable rates in the presence of either  $\text{H}_2$  or  $\text{CO}_2$ , and give therefore weight to the assumption that the primary step is represented in both cases by the rupture of a C-H bond. The successive steps of the oxidation process are represented by reactions 4.

The  $\beta_{\text{C}_2}/\bar{\tau}$  and the  $\beta_{\text{CO}}/\bar{\tau}$  plots of figure 2 are only compatible with the condition

$$k'_4 | \text{CO}_2 |, k''_4 | \text{CO}_2 | \ll k_4.$$

The rate of appearance of CO is thus determined by the rate of oxidation of the  $\text{C}_2$  intermediates, i. e., essentially by the rate of oxidation of  $\text{C}_2\text{H}_2$  by  $\text{CO}_2$ . By applying these considerations to the kinetic scheme :



values of  $k''_4$  can be derived which are of the order of  $10^9 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ . Experiments with  $\text{C}_2\text{H}_2/\text{H}_2/\text{CO}_2$  mixtures in the ratio 1/1/2, under similar discharge conditions, have shown that rate constants of acetylene oxidation are indeed of this order of magnitude, and therefore support the assumed reaction scheme.

Attention should be drawn to the fact that hydrocarbon/ $\text{CO}_2$  mixtures can almost completely be converted into  $\text{CO}/\text{H}_2$  mixtures, at kinetic gas temperatures ( $800 \pm 150 \text{ K}$ ) at which thermodynamic equilibrium would require also the presence of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and hydrocarbons. This again reflects the strong disequilibrium existing in this type of discharge, as already mentioned in the introduction, which determines both the mechanism of molecular dissociation, and the steady-state composition of the gas mixture under discharge conditions.

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