FORMATION OF CARBON DIOXIDE AND CARBON SUBOXIDE BY AN ENERGY TRANSFER PROCESS IN THE GAMMA RADIOLYSIS OF LIQUID AND SOLID CARBON MONOXIDE

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The gamma radiolysis of liquid and solid carbon monoxide-oxygen mixtures has been investigated. In the liquid phase carbon dioxide, carbon suboxide and ozone have been observed as reaction products. The formation of carbon dioxide and of carbon suboxide is to be attributed to an energy transfer process. In the solid phase the formation of carbon dioxide and ozone has been observed: the carbon dioxide is formed in part in an energy transfer reaction.

An investigation of the gamma radiolysis of liquid carbon monoxide at 77°K and of solid carbon monoxide at 20.4°K has shown that the decomposition of the carbon monoxide is strongly affected by some other gases.

In the gamma radiolysis of pure liquid carbon monoxide the reaction products found are carbon dioxide and a black-brown nonvolatile substance [1]. Contrasting to earlier suggestions, Briggs and Clay [2] have identified this product to be polymerized carbon suboxide. However, it is not possible to decide from the results of the combustion analysis by Briggs and Clay whether the solid product is pure polymerized carbon suboxide or a mixture of graphite and a polymer of unknown composition as frequently observed in the radiation chemistry of carbon monoxide [3].

An addition of oxygen, nitric oxide, ethylene or methane results in the formation of monomeric carbon suboxide instead of the polymer. In the system carbon monoxide-oxygen an increased value of $G(CO_2)$ and the formation of ozone is observed.

The results of some experiments on the gamma radiolysis of liquid and solid carbon monoxide-oxygen mixtures are given in figs. 1 - 4. The following details are important in the discussion of the system:

1. In the liquid phase at 77°K $G(CO_2)$ increases from $G_0(CO_2) = 0.23$* in pure carbon monoxide to $G(CO_2) = 0.58$ at 10 ppm (O_2) and remains nearly constant up to 3000 ppm (O_2). It should be noted that the concentration of oxygen during the radiolysis is fairly constant above 40 ppm (O_2). At 10 ppm (O_2) nearly the total amount of oxygen is consumed. Values of $G(C_3O_2)$ in various other systems at 77°K have been included in fig. 1.
2. $G(C_3O_2) = 0.10$ is constant above 40 ppm (O_2) (fig. 1).

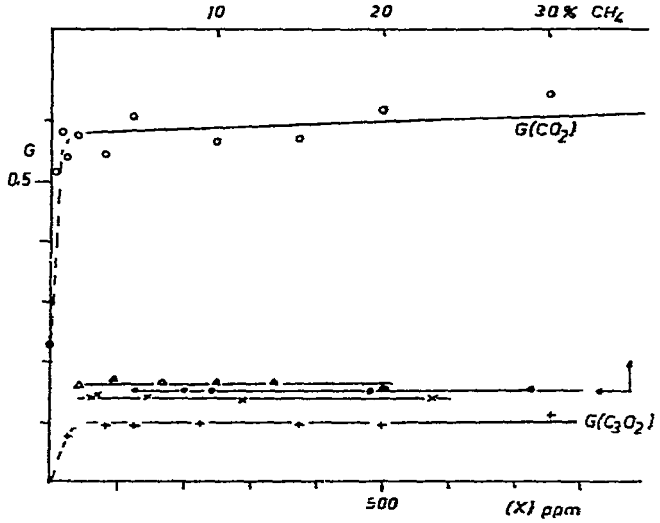

Fig. 1. Formation of CO_2 and C_3O_2 in mixtures of CO with various gases. ○$G(CO_2)$, +$G(C_3O_2)$, X = O_2. △$G(C_3O_2)$, X = C_2H_4. x$G(C_3O_2)$, X = NO. ●$G(C_3O_2)$, X = CH_4 (upper abscissa).

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* Value recalculated from ref. [1]; $G_0(CO_2) = 0.23$ is in agreement with ref. [2].

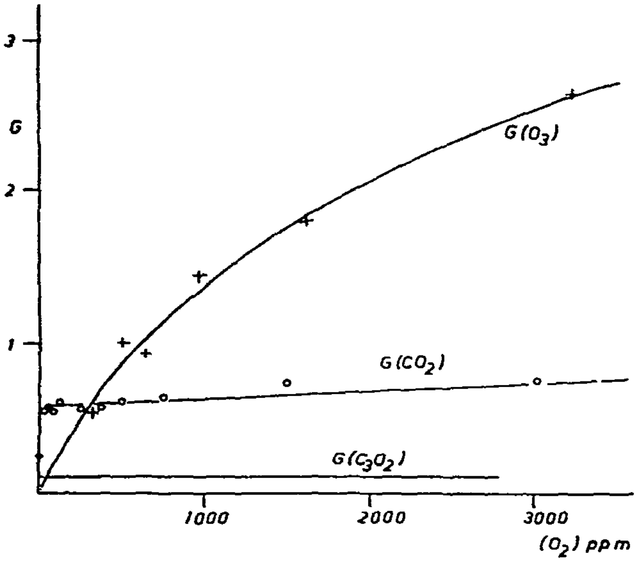

Fig. 2. Formation of CO_2, C_3O_2 and O_3 in CO-O_2 mixtures (77°K).

3. In the liquid phase the formation of ozone is independent of the formation of carbon dioxide and carbon suboxide (*fig.* 2).

However, the small increase of $G(CO_2)$ between 10 and 3000 ppm (O_2) might be due to a side reaction in the formation of ozone.

4. In the argon sensitized radiolysis of liquid carbon monoxide the relative *G*-values of the formation of carbon dioxide and carbon suboxide (defined as the ratio of the *G*-values in the system CO-Ar-O_2 to the *G*-values in the system CO-O_2) are identical (fig. 3).

5. In the solid phase at 20.4°K $G(CO_2)$ increases from $G_0^s(CO_2)$ = 0.17 in pure carbon monoxide to $G^s(CO_2)$ = 0.34 at 150 ppm (O_2). Since the slope of $G^s(CO_2)$ versus (O_2) decreases markedly at 150 ppm (O_2), the formation of carbon dioxide must be attributed to two processes (with *G*-values $G_1^s(CO_2)$ and $G_2^s(CO_2)$ respectively). Assuming that similar to the experiments in the liquid phase $G_1^s(CO_2)$ is constant above 150 ppm (O_2) $G^s(CO_2)$ can be divided into the sum $G_1^s(CO_2)$ + + $G_2^s(CO_2)$ as shown in fig. 4.

The value $G(O_3)$ in the solid phase may be taken from fig. 4. The values of $G(O_3)$ exhibit a striking parallelity to $G_2^s(CO_2)$; approximately holds $G^s(O_3)$ = 0.9 $G_2^s(CO_2)$. The formation of carbon suboxide is not observed in the solid phase.

The reactions of the various excited states in liquid and solid phase are to be investigated by photochemical means before a conclusive discussion of the results can be given. A first investigation [4] deals with the reaction of CO ($a^3\Pi$) in liquid phase. This state can be excited by the resonance line of the iodine lamp [5]. The experiments have shown that the state CO($a^3\Pi$) is quenched in pure liquid carbon monoxide and does not react with ground state molecules to form carbon dioxide and carbon suboxide as observed in gas phase. The addition of methane leads to the formation of methyl and acetyl radicals which further react forming ethane and acetaldehyde. Preliminary experiments have further demonstrated that CO($a^3\Pi$) reacts with added oxygen, probably under the formation of ozone.

The addition of oxygen, nitric oxide, ethylene or methane did not result in the formation of carbon suboxide.

The following conclusions may be drawn from the results reported in figs. 1 - 4:

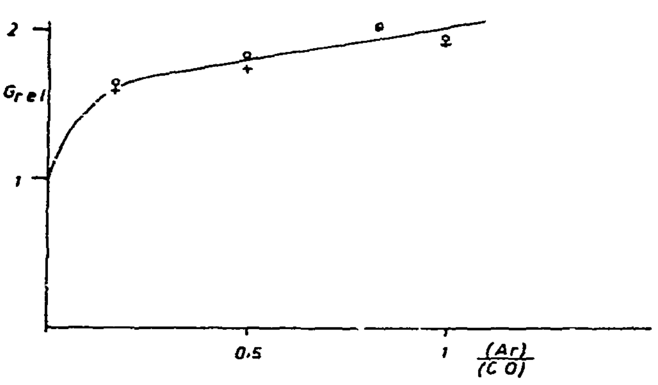

Fig. 3. Relative *G*-values of CO_2 (O) and C_3O_2 (+) in the argon sensitized radiolysis of liquid CO-O_2 mixtures. $(O_2)/(CO) \equiv 100$ ppm.

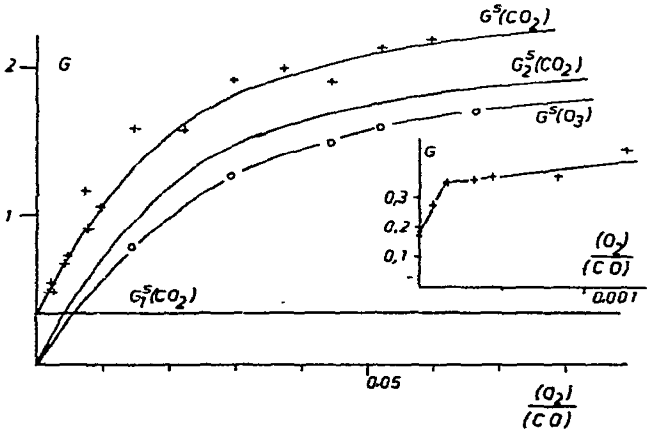

Fig. 4. Formation of CO_2 and O_3 in solid CO-O_2 mixtures.

The formation of carbon dioxide must be attributed to an energy transfer process since the energy absorbed in the oxygen is insufficient to explain the amount of carbon dioxide and since $G(CO_2)$ is nearly independent of the oxygen concentration. It is open to question in which way the energy is transferred (excitation energy, positive or negative charge) and which energy states and intermediates are involved in the reaction $O_2^* + 2\,CO = 2\,CO_2$.

The concentration of 40 ppm (O_2) corresponds to an average distance of 60 Å between a carbon monoxide and an oxygen molecule. In various other energy transfer processes distances of this order of magnitude have been observed.

On account of the results in the argon sensitized radiolysis the processes of energy transfer and of formation of carbon suboxide are to be attributed to the reaction of one single energy state of the carbon monoxide molecules.

Following Briggs and Clay [2] it may be suggested that the reaction mechanism is affected by the distribution of positive charge in the system. However, a polymerization induced by $C_3O_2^+$-ions cannot be inhibited by the addition of oxygen since the ionization potential of oxygen (I.P. = 12.1 eV) is higher than the ionization potential of carbon suboxide (I.P. = 10.8 eV) [6]. The potential precursors of carbon suboxide, C respectively C^+ and C_2O respectively C_2O^+ also have lower ionization potentials (I.P. = 11.2 and 11.4 eV respectively [6]) and cannot be discharged by oxygen molecules. The same consideration holds for methane (I.P. = 14.0 eV).

Further it is to conclude that a polymerization induced by $C_3O_2^-$-ions cannot be involved in the reaction mechanism, since ethylene which exhibits similar effects (see fig. 1) does not act as electron scavenger.

Since the change of the reaction mechanism affected by the addition of oxygen cannot be explained in terms of an inhibited polymerization, the formation of monomeric and of polymeric carbon suboxide has to be attributed to two different precursors. Those precursors may be CO-molecules, C_2O-radicals or C-atoms (respectively ions) in various states of excitation.

The close parallelity between $G(CO_2)$ and $G(C_3O_2)$ in the liquid phase indicates that the precursor of the monomeric carbon suboxide is formed in the energy transfer reaction. It is to be assumed that primary excited carbon monoxide molecules transfer a fraction of their energy to the oxygen molecules. In this process a fraction of the CO-molecules undergoes a transition to an energy state in which they react in a different manner. Another fraction of the molecules will be converted into the ground state or into a nonreactive state. The following equations will give a tentative scheme of the reaction:

$$CO \rightsquigarrow CO^* \,, \tag{1}$$

$$CO^* \xrightarrow{+\,CO} CO_2 + \text{polym.}\,, \tag{2}$$

$$CO^* + O_2 \rightarrow CO^{**} + O_2^*\,, \tag{3a}$$

$$\rightarrow CO + O_2^*\,, \tag{3b}$$

$$O_2^* + 2\,CO \rightarrow 2\,CO_2\,, \tag{4}$$

$$CO^{**} \xrightarrow{+\,3\,CO} CO_2 + C_3O_2\,. \tag{5}$$

This mechanism will give the correct stoichiometric relationship between $G(CO_2)$, $G_0(CO_2)$ and $G(C_3O_2)$. Since each primary excited CO-molecule will result in the formation of two molecules carbon dioxide (eqs. (3a), (3b) and (4)) and since one molecule carbon dioxide has to be formed for each molecule carbon suboxide in reaction (5), the relation

$$G(CO_2) = 2\,G_0(CO_2) + G(C_3O_2) \tag{I}$$

should hold. In the liquid phase the G-values are 0.58, 0.23 and 0.10 respectively.

The relation also holds in the solid phase where the formation of carbon suboxide does not take place probably on account to steric hindrance. In the solid phase eq. (I) refers to $G_1^s(CO_2)$:

$$G_1^s(CO_2) = 2G_0^s(CO_2)\,.$$

Some information about the nature of the precursors can be obtained from experiments on the gamma radiolysis of liquid carbon monoxide-methane mixtures [1]. It has been shown that monomeric carbon suboxide and acetylene are formed in a competition mechanism. Since the acetylene is formed by the reaction of carbon atoms (originating from carbon monoxide molecules) with the methane it is to assume that the precursor of the monomeric carbon suboxide is a carbon atom. On the other hand the formation of acetylene is also observed parallel to the formation of polymeric carbon suboxide. Therefore the suggestion cannot be excluded that the precursor of the polymer is also a carbon atom but of different excitation energy or of different charge.

Different potential precursors of carbon suboxide or its polymer (C-atoms and C_2O-radicals) have recently been observed in pulse radiolysis studies on gaseous carbon monoxide [7].

In the final discussion the models of energy migration and collective excitation should be taken into consideration. The formation of ozone in liquid and solid phase will be discussed elsewhere.

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