

LAWS OF THE OXIDATION OF CARBON ISOTOPES IN PLASMA PROCESSES UNDER MAGNETIC FIELD

V F Myshkin¹, E V Bepala¹, V A Khan^{1,2}, S V Makarevich¹

¹Tomsk polytechnic university, Tomsk, Russia

²V.E. Zuev Institute of Atmospheric Optics Siberian Branch of the Russian Academy of Science, Tomsk, Russia

E-mail: bepala_evgeny@mail.ru

Abstract. From law of quantum mechanics it follows that spin precession phase of unpaired electron in external magnetic field cannot be determined. It uncertainty necessary take into account in different physical and chemical processes. The expression of the rate constant of a chemical reaction based on the number of discrete spin states was obtained. The equations of chemical kinetics of plasma oxidation of carbon isotopes in the magnetic field were given.

1. Introduction

Most of the chemical element represented by two or more isotopes with different nuclear spin. Known magnetic isotope effect (MIE) - separation of isotopes with spin and spinless nuclei in chemical reactions between radicals in the liquid occurring in an external magnetic field [1]. Studies concerning the effect of the spin nuclei isotope ions изотопов ²⁵Mg, ⁵⁷Fe, ⁶⁷Zn on the rate of biochemical processes, are also developing. For example, by reacting Mg⁺ ion and ATP molecules may induce radical pairs and changes the rate of chemical reactions involving isotopes with paramagnetic nuclei [2].

Without a magnetic field, the spatial orientation of the spin is not determined and all the spin orientations are equally probable. Valence electron spin precession relative to the direction of the magnetic field is observed in the magnetic field. This reduces the number of possible combinations of mutual spatial orientation of the colliding radicals. Also, the rate of change of physical and chemical processes is observed [3]. On the conditions of formation of a chemical bond between the two radicals influenced by two factors: the energy and spin [1]. The influence of magnetic field on the gas-phase chemical reactions received little attention.

The purpose of the study is the analysis of paramagnetic effects in low-temperature plasma, placed in an external magnetic field.

2. Paramagnetic phenomena in the gas system

When the diffusion of radicals into the liquid in a magnetic field and it is possible to capture radicals in "cage." At the same time there are 4 states: one singlet and three triplet. Spin pair multiplet can be configured in 3 ways: oppositely directed, co-current up or down. Possible combinations of spins are shown in Figure 1. Due to the cage effect in the liquid main factor controlling the reactivity of radicals in the external magnetic field is a dynamic spin pairs.

Approaches used for liquid-phase reactions, but for gas-phase reactions are not suitable. Currently, the ability to influence paramagnetic phenomena on the gas-phase chemical reactions, because of the



much greater value of the conversion time of spin pairs compared to the time of initial contact radicals are not considered.

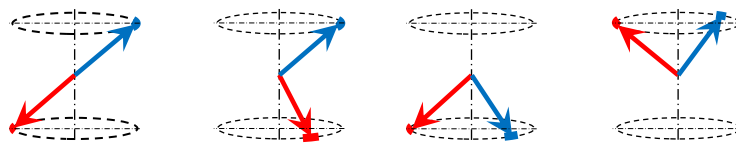


Figure 1. Scheme of forming different states of multiplet

It is considered that due to the statistical independence of the spatial orientation of the spins of the colliding radicals diffusion couples (uncorrelated) the probability of different states of a spin multiplet is identical and equal to 25% [4]. This is due to the indistinguishability of various phase states of the precession of the spin with the direction of $+1/2$ or $-1/2$ with respect to the external magnetic field, such as in the experiments of Stern and Gerlach. The interaction of the back of the multiplet considered in parallel planes or in one plane.

In quantum mechanics, the electron state, for example, spin "up" $+1/2$ denoted as state vector $|+1/2\rangle$, which involves degeneration of the condition. The states of the multiplet can be formed spins of electrons in different planes (having different phases of the valence electron spin precession) (see Figure 1). At the same time singlet state can only occur in the case of coincidence of the two planes of the spins and the triplet state - for any combination of these planes spins. It is obvious that in gas phase the probability of formation of various states of the multiplet depends on difference realizations of angle dispositions with spin precession of forming spin pairs ($|+1/2\rangle$, $|+1/2\rangle$).

The uncertainty relation for S_x and S_y projection of the spin operator can be written in the form of expression $\Delta S_x \Delta S_y \geq \hbar/2 |\langle S_z \rangle|$. Under the condition $\langle S_z \rangle = \hbar/2$ with dispersion $\Delta S_z = 0$ we obtain $\Delta S_x \Delta S_y \geq (\hbar/2)^2$. Under the same conditions, the dispersion of the spin operator of projection on the axis OX and OY ($\Delta S_y \approx \Delta S_x$) we get $\Delta S_x \geq \hbar/2$.

Estimation algorithm $\Delta\varphi$ values of trigonometric ratios demonstrated by Figure 2.

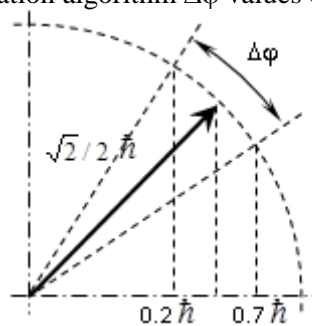


Figure 2. Scheme of estimation uncertainty phase of the spin precession.

Estimation algorithm $\Delta\varphi$ values of trigonometric ratios demonstrated by Figure 2. The value $\Delta S_x \geq \hbar/2$ at different limit values can be implemented as: $\Delta S_x = (0.7-0.2)\hbar$ and $\Delta S_x = [0.25-(-0.25)]\hbar$. Accordingly, the uncertainty (discrete) $\Delta\varphi$ the angle of spin precession in the range $73.4^\circ-41.4^\circ$. Can be distinguished $n = 2\pi/\Delta\varphi$ ranges phase at the valence electron spin precession radical realized in various physical and chemical processes as "discrete" states. In the range $\Delta\varphi \approx 41.4^\circ \div 73.4^\circ$ mean value is 57° ; and the mean value of n is $n \approx 6.3$.

Consideration uncertainty of phases of spin precession, for one of the radicals can be detected n singlet states S at its collision with the second radical with axisymmetric spin direction. At the same time state S can be considered as a special case of the state of T_0 . Triplet states can be implemented as follows: $T_0 - n(n-1)$; but T_{-1} and T_{+1} states as combinations of n «up» with n states «down» – n^2 spin position of colliding radicals. The probability of formation of the singlet state at the next collision of all possible sets of interacting spins is:

$$\delta S = \frac{[S]}{[S + T_0 + T_{-1} + T_1]} = \frac{n}{n + n(n-1) + 2n^2} = \frac{1}{3n}. \quad (1)$$

Therefore, the proportion of singlet states of all possible set of interactions of the spins of radicals is $1/3n$ or 5.3%, but not 25%.

3. The gas-phase chemical reaction between the radicals in the magnetic field

In the gas-phase processes each $3n$ radicals collision with a 100% probability may be terminated form reaction products. The frequency of the formation of the singlet state in a collision radicals in the external permanent magnetic field, taking into account the frequency of collisions of particles per unit volume of gas can be written as (2):

$$v_s = \frac{1}{3n} \frac{\sqrt{2}}{2} \bar{v} \sigma [R1][R2] \quad (2)$$

where $R1, R2$ – concentrations of the two types of radicals, \bar{v} – the mean relative velocity of thermal motion, σ – effective cross section of collision of two types of radicals.

However, equation (2) does not consider the possibility of collapse resulting in an excited state of a new molecule. When taking into account short lifetime of the radiative relaxation of excited states, the equation (2) can be considered valid.

The equation of the second order chemical reaction is proportional to the product of the concentrations of the reactants involved:

$$\frac{d[R1]}{dt} = v_s = k [R1][R2]. \quad (3)$$

From a comparison of the expressions (2) and (3) shows that the rate constant of a chemical reaction can be written as expressions:

$$k = \frac{1}{3n} \frac{\sqrt{2}}{2} \bar{v} \sigma. \quad (4)$$

To estimate the rate constant of the oxidation of carbon in the low-temperature plasma will take the relative velocity at 1500°C $\bar{v} \approx 3 \cdot 10^5$ cm/s and the effective collision cross section is $\sigma \approx 5 \cdot 10^{-15}$ cm². As a result, we obtain the estimate $k \approx 16.8 \cdot 10^{-11}$ cm⁶/s. This value is close to the experimental value ($5.22 \cdot 10^{-11}$ cm⁶/s) for the reaction of carbon oxidation at 1500 K at pressures of 0.5-1.2 atm [5]. The difference in the reaction constant may be related to the oxidation reaction of carbon by several ways, and we estimate inflated sectional collision.

In general, the isotope effect of radical processes in the gas phase is determined by the kinetic energy and the distribution of the excited levels for reactions with different thermal effect. The collision frequency determined by the arithmetic average rate determined from the Maxwell velocity distribution of particles of the thermal motion:

$$\Delta N = N \frac{4}{\sqrt{\pi}} \frac{v^2}{v_{prob}^2} \frac{\Delta v}{v_{prob}} \exp\left[-\frac{v^2}{v_{prob}^2}\right], \quad (5)$$

where v – particle velocity, k – Boltzmann constant, T – temperature.

If you exceed the reaction threshold of faster particles collide more often. Therefore, the formation of chemical bonds have a higher probability. Without a magnetic field, both isotopes have the same and constant in time the probability of the formation of singlet pairs. The molecules formed from the fast particles have a greater excess of energy, and consequently have a higher probability of spontaneous collapse.

Expression (2) can be written for each pair of components of the Maxwell velocity distribution.

For the analysis of rates of chemical reactions with the participation of different isotopes, having

different velocity distribution of thermal motion can be use the expression for the formation frequency of singlet states, compiled for a discrete analogue of the Maxwell distribution of velocities:

$$v_s = \frac{\sqrt{2}}{6n} \sum_{i=1}^n \left(\sum_{j=1}^m \sigma_{12}^j v_{12}^j N_1^{ij} N_2^{ij} \right), \quad (6)$$

where m – the number of discretization of the Maxwell velocity distribution, n – the number of discretization phase of the precession of the spins of valence electrons is the same for both radicals, v_{12} – the relative velocity of the colliding radicals, N_1^{ij} , N_2^{ij} – radical concentration with the given values phase precession of the electron spin and the velocity of the radical, σ_{12}^j – cross section of collisions of particles with a relative velocity v_{12}^j .

4. The kinetics of plasma oxidation of carbon isotopes under the magnetic field

Under the conditions of the plasma for describing of chemical kinetics used Pauli equation that takes into account the distribution of the atoms of the reactants electronically excited states. [6]. Given the high content of atoms in excited states is necessary to take into account the contribution of the chemical reaction of the excited states, differing in the value of the g-factor. In a magnetic field, the spin precession frequency, except the g-factor, also determines the spin of the nucleus.

In [7-9] it showed enrichment ^{13}C in products of incomplete oxidation of carbon plasma in a magnetic field. Oxidation ^{12}C and ^{13}C in a low-temperature plasma, using equation (6) can be described by the following equations.

1. The oxidation of the carbon isotope ^{12}C (^{13}C) by molecular (or atomic) oxygen:

$$\frac{d[^{12}\text{CO}]}{dt} = \frac{\sqrt{2}}{6n} \sum_{i=1}^n \left(\sum_{j=1}^m (\sigma_{12\text{C}-\text{O}_2}^j v_{12\text{C}-\text{O}_2}^j N_{\text{O}_2}^{ij}(t) N_{^{12}\text{C}}^{ij}(t)) \right), \quad (7)$$

2. Equation for computation of decline rate of molecular (atomic) oxygen in the oxidation of carbon isotopes ^{12}C , ^{13}C :

$$\frac{d[\text{O}_2]}{dt} = - \frac{\sqrt{2}}{6n} \sum_{i=1}^n \left(\sum_{j=1}^m (\sigma_{^{13}\text{C}-\text{O}_2}^j v_{^{13}\text{C}-\text{O}_2}^j N_{\text{O}_2}^{ij}(t) N_{^{13}\text{C}}^{ij}(t)) \right) - \frac{\sqrt{2}}{6n} \sum_{i=1}^n \left(\sum_{j=1}^m (\sigma_{^{12}\text{C}-\text{O}_2}^j v_{^{12}\text{C}-\text{O}_2}^j N_{\text{O}_2}^{ij}(t) N_{^{12}\text{C}}^{ij}(t)) \right), \quad (8)$$

where N_{O_2} , $N_{^{13}\text{C}}$, $N_{^{12}\text{C}}$ – the concentration obtained by discretization of the Maxwell distribution of m velocities of and n discrete states precession phases for O_2 , ^{13}C , ^{12}C .

3. On isotopic selectivity of CO oxidation by molecular (atomic) oxygen, the magnetic field has no effect (CO molecule has no unpaired electrons):

$$\frac{d[\text{CO}_2]}{dt} = \frac{\sqrt{2}}{6n} \sum_{i=1}^n \left(\sum_{j=1}^m (\sigma_{\text{CO}-\text{O}_2}^j v_{\text{CO}-\text{O}_2}^j N_{\text{O}_2}^{ij}(t) N_{\text{CO}}^{ij}(t)) \right). \quad (9)$$

Uniform phases of spin precession state is maintained collisions which do not result in the formation of chemical bonds. The spin-spin relaxation occurs when collisions with atoms of plasma-forming gas.

Isotopes of same elements differ from g and a . Therefore for each isotopes it is typical the time of occurrence of valence electron of radical in one of range of uncertainty $\Delta\varphi$ in the angles of the precession:

$$\Delta t = \frac{h}{n g \mu_B (H + a)}. \quad (10)$$

Depending of collision frequency, which depend on pressure and temperature, radicals of two reactants collide step-by-step in different precession phases of their valency electron spin. Besides probability of formation of singlet stage as a result of each collision of two radicals change according

to harmonic law [10]. Oscillation frequency of chemical activity is difference between collision frequency of radicals and frequency of paramagnetic resonance of two radicals. Two reactants undergo a chemical reaction every $3n$ collision with probability 1.0. Under certain conditions for two isotopes possible isotopes effects of carbon oxidation in external field. For example, equality collision frequency of one isotopes of carbon with oxygen with difference frequency of paramagnetic resonance of it isotope and oxygen.

5. Conclusion

Spin precession in a magnetic field should be considered for discrete angular coordinate during consideration different physical and chemical processes. Therefore constant of chemical reaction between radicals in external permanent magnetic field can calculate from collision frequency, which depend on gas kinetic parameters of radicals, temperature and pressure of gas. Besides theoretical assessment of constant of oxidation rate of each carbon isotopes and isotope effect of chemical reaction in external permanent magnetic field.

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