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CONDITIONS OF FORMATION OF μ^+-MESIC MOLECULES

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The formation of μ^+-mesic molecules in interactions between muonium and organic molecules is considered. The experimental conditions for the expected formation of μ^+-mesic molecules and μ^+-mesic radicals are determined and a possible observational procedure is indicated.

1. Ansel'm and Shekhter[1] have recently considered a very interesting possibility for the production of μ^+-mesic molecules, basing their calculation on the theory of an activated complex for the reaction between a muonium atom and a hydrogen molecule. They assume (I) that μ^+-mesons in a medium capture electrons long before they can decay and are transformed into muonium, which (II) then is thermalized, and (III) that the electronic structure of muonium resembles that of hydrogen except for certain effects that can be neglected in the present case.

In this paper the rates of μ^+-mesic molecule formation are determined in the gaseous and condensed phases of several organic molecules, and the minimum temperatures for the experimental observation of μ^+-mesic molecules are calculated. The aforementioned three assumptions are retained, the third of which is obvious, while the other two are confirmed qualitatively for sufficiently dense media by radiochemical experiments with hot hydrogen atoms.

Unlike[1], the muonium reaction rate constants are not calculated directly, but are determined from corresponding experimental data for hydrogen reactions. A correction, required mainly because of the mass difference, is calculated using the theory of the so-called kinetic isotope effect.[2,3] In addition, we take into account the tunnel effect, whose role becomes more important because of the relatively small muonium mass. This procedure yields more accurate results and enables exclusion, to a considerable extent, of unknown parameters in the activated complex theory.

Special attention is devoted to the production of μ^+-mesic radicals, which are systems that include an unpaired electron and can be detected with high accuracy.

2. We shall assume the realization of a steady flux of thermalized muonium (μ^+e) atoms reacting in organic matter to form μ^+-mesic molecules. Under the conditions considered below (gases at atmospheric pressure and the condensed phase) the ratio of the μ^+-mesic molecule concentration ρ_1 to the total μ^+-meson concentration ρ will in each case be given by

$$\rho_1/\rho = k_1/(k + k_1), \tag{1}$$

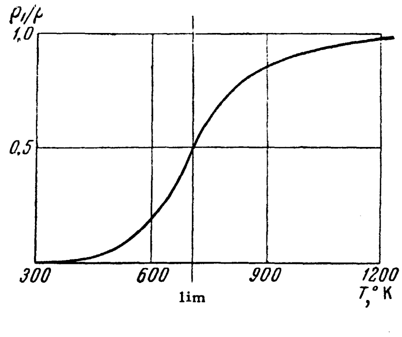
where k and k_1 are the probabilities per unit time of μ decay and of mesic molecule formation from muonium alone.

The quantity k_1 is, by definition, the usual chemical rate constant of the bimolecular reaction,[2] multiplied by the concentration [C] of the substance C with which the muonium reacts. The ratio (1) can, in principle, be determined experimentally from measurements of μ^+-meson depolarization.[4] The strong temperature dependence of k_1 can be represented by[2]

$$k_1 = k_0 \, [C] \exp(-E_{\text{exp}}/RT), \tag{2}$$

where E_{exp} is the experimental activation energy per mole, defined as the derivative of $\ln(k_1/[C])$ with respect to $-1/RT$; k_0 is the preexponential factor.

Both k_0 and E_{exp} are relatively weakly temperature dependent. In accordance with (2), Eq. (1) has the temperature dependence represented in the



Dependence of ρ_1/ρ on absolute temperature in the reaction of muonium with methane. The methane concentration is 2.5×10^{19} molecules/cm³.

figure for a reaction with gaseous methane having the parameters computed below. In plotting this curve it was assumed that the methane concentration is maintained constant and equal to the concentration at atmospheric pressure and room temperature.

The figure shows the existence of a large temperature interval in which most of the muonium can form μ^+-mesic molecules. This interval can be characterized by a temperature $T_{\lim}$ determined from the condition

$$p_1/p = 1/2 \text{ or } k_1(T)/k = 1. \tag{3}$$

From (2) and (3) with a concentration [C] that varies sufficiently slowly with temperature, we obtain

$$T_{\lim} = E_{\exp}/R \ln (k_0 [C]/k). \tag{4}$$

Let us consider a characteristic of Eq. (4). $T_{\lim}$ is proportional to $E_{\exp}$ and depends weakly on another quantity, k_0, which is to be determined. For a sufficiently accurate value of $T_{\lim}$ the value of k_0 must be determined only to within the order of magnitude (with logarithmic accuracy, as will be stated subsequently). The approximate equations given below will correspond to this or better accuracy.

3. The determination of $E_{\exp}$ and k_0 will in each case be based on the experimental rate constant k_1^H of hydrogen atom reactions. It will be necessary to calculate

$$\chi = k_1/k_1^H. \tag{5}$$

This calculation, which will be based on equations for the isotope effect in the so-called activated complex theory,[2,3] yields, as already stated, considerably more accurate results than a direct calculation for a gaseous medium and enables reasonable estimates for condensed media.

The calculation will employ the approximate picture (to be described below) of the geometric structure of an activated complex. This is justified, first of all, by the sufficiency of logarithmic accuracy in determining k_0 and is in accord with concepts used in the modern chemical theory of reaction rates.[5] It will be assumed that an activated complex is a loose structure with a relatively large separation between the added muonium (or hydrogen) and the heavier organic molecule that practically preserves its own structure. The reaction between muonium and hydrogen requires certain additional corrections.

In accordance with the foregoing it can be assumed that two additional low-frequency vibrations associated with the formation of an activated complex (a third additional vibration being included in the so-called reaction degree of freedom[2]) are transverse relative to the direction of the formed bond, and that their frequencies for the muonium reactions are to the corresponding frequencies for hydrogen reactions approximately as the square roots of the reciprocal of the reduced mass ratio

$$\alpha \equiv \nu_\mu/\nu_H \cong [m_H (m_C + m_\mu) / (m_C + m_H) m_\mu]^{1/2} = 3 - \Delta. \tag{6}$$

Here it must be emphasized that the inaccuracy in the given picture of activated complex structure leads to an error of less than 10° in $T_{\lim}$, which is considerably smaller than the error associated with the limited applicability of the activated complex method. According to the activated complex theory (p. 173 of [2]), with the assumed ideas regarding the structure of the complex in the present case, we have

$$\chi = \frac{Z^{C\ldots\mu} Z^H}{Z^{C\cdots H} Z^\mu} \exp\left[-\frac{2N}{RT}\left(\frac{h\nu_\mu}{2} - \frac{h\nu_H}{2}\right)\right], \tag{7}$$

where $Z^{C\ldots\mu}$, $Z^{C\ldots H}$, Z^H, and Z^μ are the statistical sums of activated complexes formed with muonium and hydrogen (without "reaction vibrations"), and of hydrogen and muonium. We here distinguished the shifts of the two zero-point vibration energies in the activation energy and considered the reactions to be adiabatic with transmission coefficients not differing from unity.[2,3,5] We have thus far not taken into account the possible influence of the tunnel effect in overcoming the potential barrier; this will be discussed in Sec. 4.

The ratios in (7) can be written as

$$Z^H/Z^\mu = (m_H/m_\mu)^{3/2}, \tag{8}$$

$$\frac{Z^{C\ldots\mu}}{Z^{C\ldots H}} = \beta \frac{(m_C + m_\mu)^{3/2}}{(m_C + m_H)^{3/2}} \left(\frac{J_1^{\mu\ldots C} J_2^{\mu\ldots C} J_3^{\mu\ldots C}}{J_1^{H\ldots C} J_2^{H\ldots C} J_3^{H\ldots C}}\right)^{1/2} \times \frac{(1 - \exp(-Nh\nu_H/RT))^2}{(1 - \exp(-Nh\nu_\mu/RT))^2}. \tag{8'}$$

In (8′) the coefficient β accounts for the possible effect of the difference between muonium and hydrogen; it differs from unity, being equal to 2 in the cases C = H and H_2. $J_1J_2J_3$ denotes the product of the moments of inertia.

We now use the Redlich-Teller theorem[2,6] according to which for a molecular system of k atoms the ratio

$$\left(\sum_k m_k\right)^{3/2} (J_1 J_2 J_3)^{1/2} / \prod_i \nu_i \prod_k m_k^{3/2}$$

is independent of the atomic masses; here $\prod_i \nu_i$

is the product of the frequencies of the normal vibrations. By means of this theorem, utilizing the foregoing ideas regarding the structure of the complex together with Eq. (6), we obtain

$$\frac{Z^{C\ldots\mu}}{Z^{C\ldots\mathrm{H}}} = \alpha^2\beta\,\frac{\nu^{C\ldots\mu}}{\nu^{C\ldots\mathrm{H}}}\frac{m_\mu^{3/2}}{m_\mathrm{H}^{3/2}}\left(\frac{1-\exp\left(-Nh\nu_\mathrm{H}/RT\right)}{1-\exp\left(-Nh\nu_\mu/RT\right)}\right)^2. \quad (9)$$

The ratio of the imaginary (p. 174 of [2]) frequencies of "reaction vibrations" $\nu^{\mathrm{C}\ldots\mu}/\nu^{\mathrm{C}\ldots\mathrm{H}}$ is inversely proportional to the ratio of the square roots of the masses corresponding to these vibrations. Developing Slater's ideas [7] supported by results obtained from investigations of isotope effects in hydrogen and deuterium reactions, we can consider that, for example, in the substitution reactions discussed below with the formation of $\mu^+\mathrm{H}$ and H_2 from the organic molecules C, these masses will be the reduced mass of the muon-hydrogen system in one case, and of the system of two hydrogen molecules in the other case. Accordingly,[1]

$$\left(\frac{\nu^{C\ldots\mu}}{\nu^{C\ldots\mathrm{H}}}\right)_{\mathrm{sub}} \cong \sqrt{\frac{m_\mathrm{H}+m_\mu}{2m_\mu}}. \quad (10)$$

Substituting (8), (9), and (10) in (7) we obtain for the substitution reaction

$$\chi = \alpha^2\beta\sqrt{\frac{m_\mathrm{H}+m_\mu}{2m_\mu}}\left(\mathrm{sh}\,\frac{Nh\nu_\mathrm{H}}{RT}\Big/\mathrm{sh}\,\frac{Nh\nu_\mu}{RT}\right)^2. \quad (11)^*$$

In the temperature interval 500–700°K that includes T_{lim} for gases, χ depends only weakly on temperature and therefore does not contribute to a difference between E_{exp} for hydrogen atom reactions and muonium reactions. This results from the following calculations. For substitution reactions $Nh\nu_\mathrm{H}/2R$ lies within the interval 200–300°. [5]

Since for almost all the temperatures of interest we have

$$|\Delta Nh\nu_\mathrm{H}/2RT| \ll 1, \quad (12)$$

we obtain through simple transformations involving (6)

$$\chi_{\mathrm{sub}} = \alpha^2\beta\sqrt{\frac{m_\mathrm{H}+m_\mu}{2m_\mu}}\left(\alpha + 4\,\mathrm{sh}^2\,\frac{Nh\nu_\mathrm{H}}{2RT}\right)^{-2}. \quad (13)$$

Above $Nh\nu_\mathrm{H}/2R$, Eq. (13) depends only slightly on temperature; we can write in general with logarithmic accuracy

$$\chi \cong \beta\sqrt{(m_\mathrm{H}+m_\mu)/2m_\mu} \cong 2.2\,\beta. \quad (14)$$

An additional coefficient of the order of unity can appear in (14) as a result of the tunnel effect (see below).

Thus when T_{lim} is calculated from (4) for reactions in gases we can simply substitute $E_{\mathrm{exp}} = E^{\mathrm{H}}_{\mathrm{exp}}$ and only slightly corrected values, in accordance with (14), of the preexponential factor k_0^{H} for hydrogen atom reactions.

The accompanying table gives computed values of T_{lim} above 500°K for several substitution reactions producing $\mu\mathrm{H}$. An estimate is also given for an addition reaction with a double bond in the case of ethylene; this reaction can begin to occur at room temperature. It should be noted that in this case the depolarization of μ^+ mesons will be relatively accelerated through an interaction with the unpaired electron that is present in the formed radical.

4. We shall now consider reactions in the condensed phase. This can generally be considered in principle analogously with the procedure used for reactions in gases. Since in this case reactions producing mesic molecules occur at low temperatures, we must here also consider the possible influence of the tunnel effect in overcoming the potential barrier in an activated complex. Since the mass of muonium is much smaller than that of hydrogen, the tunnel effect should here in principle be considerably more important.

According to Wigner's theory [2,9] the tunnel effect will be taken into account sufficiently if we multiply the calculated reaction rate constant k_1 by

$$1 + \tfrac{1}{24}\left(Nhi\nu^{C\ldots\mu}/RT\right)^2, \quad (15)$$

where $\nu^{\mathrm{C}\ldots\mu}$ is, as in (9), the imaginary frequency of reaction vibrations.

From the form of the potential surface we estimate $Nhi\nu^{\mathrm{C}\ldots\mu}/R\sqrt{24} \sim 1000°$ in reactions with organic molecules. From (10) the corresponding value for hydrogen reactions is smaller by the factor 2.2. Thus, in contrast with the usual chemical kinetics, the tunnel effect can play an appreciable part in muonium reactions. This fact, together with the effect of the temperature-dependent factor (13), should be manifested at low tempera-

T_{lim} for muonium reactions in gases having a constant concentration $[\mathrm{C}] = 2.5 \times 10^{19}$ molecules/cm^3

Reaction	$E^{\mathrm{H}}_{\mathrm{exp}}/R$, °K [8]	T_{lim}, °K
$\mu + \mathrm{CH}_4 \rightarrow \mathrm{CH}_3 + \mu\mathrm{H}$	5500	700
$\mu + \mathrm{C}_2\mathrm{H}_6 \rightarrow \mathrm{C}_2\mathrm{H}_5 + \mu\mathrm{H}$	4500	580
$\mu + \mathrm{C}_3\mathrm{H}_8 \rightarrow \mathrm{C}_3\mathrm{H}_7 + \mu\mathrm{H}$	4350	560
$\mathrm{C}_2\mathrm{H}_4 + \mu \rightarrow \mathrm{C}_2\mathrm{H}_4\,\mu$	1200	~250

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[1] In all cases (10) is the upper limit of the corresponding ratio.

*sh = sinh.

tures in the form of a deviation from the Arrhenius law.[10]

In line with the foregoing, the reaction rates of muonium in condensed phases should agree with the rates of the corresponding chemical reaction rates of hydrogen to within an order of magnitude (or somewhat better). Since the latter reaction rates are also known only to within an order of magnitude they can be substituted directly in (1) for an estimate of ρ_1/ρ. The results obtained by this substitution for reactions in liquids (at 296°K) based on Hardwick's data[11] are:

Reaction	$1-\rho_1/\rho$
1) $C_6H_{14} + \mu \rightarrow \mu H + C_6H_{13}$	0.02
2) addition of muonium to benzene	4×10^{-6}
3) ” ” ” to ethylbenzene	1.5×10^{-6}
4) ” ” ” to diphenyl	1×10^{-6}
5) ” ” ” to paraterphenyl	5×10^{-7}

It is thus seen that in a condensed medium practically all μ^+ mesons must form μ^+ mesic molecules at room temperature. Reactions 2—5 represent addition to aromatic molecules including organic scintillators such as paraterphenyl. As already mentioned, in such addition reactions the depolarization of μ^+ mesons will depend on the interaction with the unpaired electron of the corresponding radical.

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