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Reaction of Anthracene with CH Radicals: An Experimental Study of the Kinetics between 58 and 470 K[†]

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The rate coefficient of the reaction of the methylidine radical CH with anthracene has been studied over a wide temperature range (58−470 K) in a dedicated “Cinétique de Réaction en Ecoulement Supersonique Uniforme” (Reaction Kinetics in Uniform Supersonic Flow) apparatus. The reaction exhibits a slight positive temperature dependence, which can be fitted to the expression $k(T) = (3.32 \pm 1.00) \times 10^{-10}(T/298)^{(0.46\pm0.14)}$ cm^3 molecule^{-1} s^{-1}. Even at the lowest temperature, the reaction remains very fast indicating that the kinetics are probably driven by a capture process.

1. Introduction

During the past decade the understanding of the complex chemistry that occurs in the Universe has become a fascinating challenge for scientists. Cold and ultracold media, partly or totally shielded from harsh radiation fields, such as dense and diffuse interstellar clouds and planetary atmospheres of the outer solar system provide the most favorable environment for the appearance of this chemistry. Evidence for the presence of extraterrestrial complex organic molecules was found a long time ago in some meteorites,[1] and today more than 125 circumstellar and interstellar molecules have been detected. Recently, the European Space Agency’s Huygens probe descended through the cloudy atmosphere of Saturn’s main moon, Titan, and will soon furnish the first direct measurement of chemical species in extraterrestrial atmospheres.[2]

Among this wealth of chemical species, polycyclic aromatic hydrocarbons (PAHs) are suspected to have a significant place in the chemical scheme of these cold media. In their neutral or ionic forms, PAHs have been detected[3] in meteorites and thought to be present in interstellar clouds, where PAH cations could be good candidates as the carriers of the diffuse interstellar bands.[4,5] In planetary atmospheres, these large molecules are cited by Wilson et al.[6] as one of the ways for production of Titan’s haze, which hide the moon’s surface from direct Earth observations. The presence of PAHs in Titan’s atmosphere has been discussed by Sagan et al.[7] and more recently by Trainer et al.[8] At low temperatures (interstellar medium, planetary atmosphere) similar to high temperatures (circumstellar envelopes) the formation of PAHs is predicted to involve the chemistry of benzene[9,10] (C_6H_6). Benzene is the first aromatic compound that has been detected by ISO (Infrared Space Observatory) in carbon-rich stars[11] and also in Jupiter and Saturn.[12] In recent observations Coustenis et al.[13] have found evidence for C_6H_6 on Saturn’s main moon and pointed out the significant role of aromatic compound for gas-phase chemistry at low temperature. Despite the importance of aromatic compounds, there are only few laboratory studies of reactions with benzene or PAHs in their neutral form[14−16] and only one direct measurement of a radical−PAH reaction has been performed at low temperature.[17] To understand the basic chemistry of such species, it is necessary to study experimentally and theoretically elementary reactions of PAHs with radicals involved in the chemistry of interstellar media or planetary atmospheres.

In the atmosphere of outer planets and their satellites, small carbon-containing radicals such as methylidine are produced by methane photolysis, mainly by the Lyman-α solar flux. It follows that the significance of the radical in these atmospheres is directly linked to the quantum yield for its formation in the photodissociation of methane at 121.6 nm. However, recent studies have not been able to resolve the issue of methane photolytic yields at this wavelength. The measurements of Rebbert and Ausloos[18] indicated a rather small value, close to 0.08. Mordaunt et al.[19] suggested a larger value of about 0.5. More recently Romani[20] and Smith and Raulin[21] gave values of 0.1 and 0.06, respectively. To investigate the significance of these quantum yield schemes on the hydrocarbon chemistry of Titan’s atmosphere, Wilson and Atreya[22] have used a one-dimensional photochemical model. They showed that the methane photolysis quantum yield does not affect the abundance of important hydrocarbons such as acetylene (C_2H_2) or ethylene (C_2H_4). Only minor three-carbon-atom molecules are sensitive to the choice of the methane photolysis quantum yield. The nominal value seems to be the Romani’s value of 0.1. Previously, Canosa et al.[23] argued that a low value would imply a barrier to the formation of $CH + H_2$ in the unimolecular decay of the superexcited CH_3 fragments which are formed in photolysis of CH_4, which is unlikely on the basis of both ab initio calculations[24] and kinetic results for the reaction and relaxation of CH($v = 0$) and CH($v = 1$) in collisions with H_2 and D_2 at ultralow temperatures.[25] It should be noted that a large quantum yield for production of CH in the photolysis of CH_4 had earlier been deduced from the experimental work of Braun et al.[26] It follows that the methylidine radical could have a central place in the chemistry of several planetary atmospheres.

It might also be noted that CH was one of the first molecules detected in the interstellar medium,[27,28] in diffuse clouds where it plays a vital role in the gas-phase chemistry.[29−31] In dense

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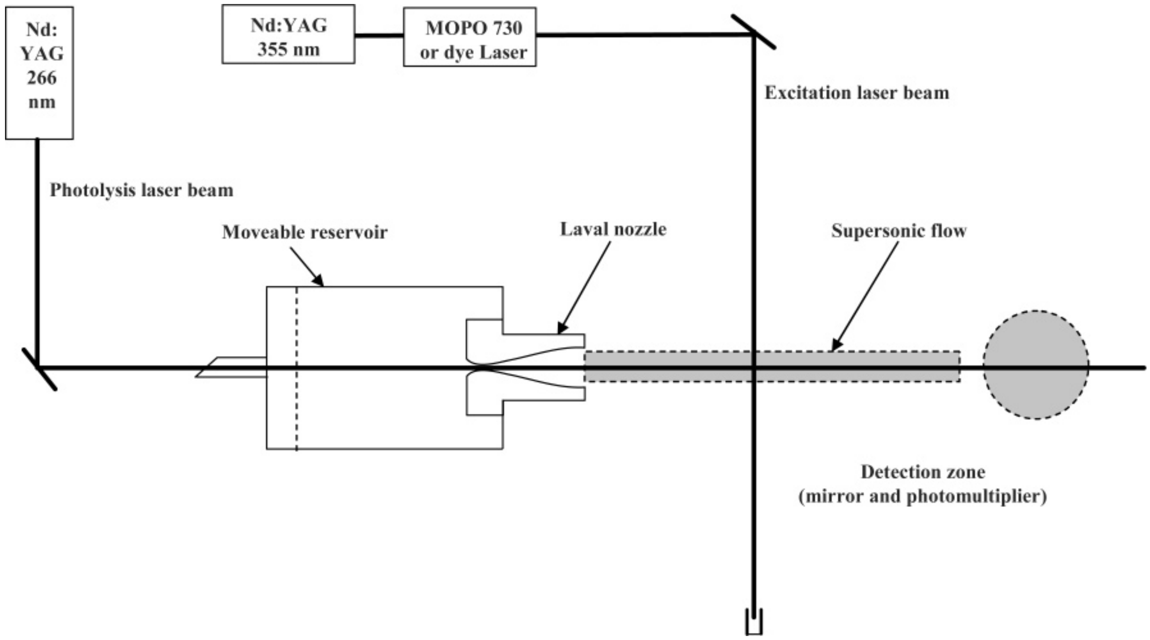


Figure 1. Schematic view of the CRESU apparatus.

clouds, although certainly of much less importance than the corresponding reactions with neutral and ionized atomic carbon, reactions of hydrocarbons with the methylidine radical can lead to the accretion of carbon to produce a larger carbon skeleton, opening the way to the formation of large organic molecules.[32]

The database on the kinetics of neutral−neutral reactions has been improved during the past decade due to the progress made in theoretical calculation and experimental measurements. Rate coefficients at low temperature have been measured using the well-known "Cinétique de Réaction en Ecoulement Supersonique Uniforme" (CRESU, Reaction Kinetics in Uniform Supersonic Flow) facility at the University of Rennes I and Birmingham. The apparatus at the University of Rennes I is the only one capable of measuring the rate coefficient of reactions involving PAHs at temperatures relevant to the interstellar medium.[17]

In this paper, we present the result for the first rate coefficient measurement of the CH radical reaction with anthracene ($C_{14}H_{10}$) between 58 and 470 K. We have used a modified CRESU apparatus dedicated to the study of gas-phase chemistry involving condensable molecules.[17] The measured rate coefficient is found to be close to the gas kinetic rate coefficient and shows a positive evolution with the temperature. The high value of the rate coefficient even at 58 K shows the importance of this kind of reaction for the chemistry of low temperature media. The knowledge of the nature of the products would also be of vital importance but will only be discussed below, since our experiment does not yet allow reaction products to be determined.

2. Experimental Section

The results presented in this paper were obtained by using the modified CRESU apparatus that has been developed at the University of Rennes I. The basis of the technique and the modifications due to the use of PAHs have been described in detail elsewhere,[17] and only a concise description will be given here. A general sketch of the apparatus is given in Figure 1.

Low temperatures are achieved in the CRESU apparatus via the isentropic expansion of a buffer gas through a suitably designed Laval nozzle. The resulting supersonic flow is axially and radially uniform in temperature, density, and velocity. The density of the flow ($10^{16}-10^{18}$ cm^{-3}) is large enough to ensure local thermal equilibrium by collisions. To use low vapor pressure compounds, a special apparatus has been developed, in which the reservoir is heated at 470 K by circulating heated oil from a bath regulated in temperature (Lauda CS20CS) through the double-jacketed walls of the reservoir. The aluminum laval nozzle is embedded in a conical hollow aluminum support mounted on the reservoir and heated by thermal conduction. Several aluminum nozzles have been designed for this experiment, each providing a particular temperature and density for the selected carrier gas. It is also possible to generate a subsonic flow, whose temperature is the same as the temperature of the reservoir. All nozzles were characterized by impact-pressure (Pitot) measurements from which the Mach number, temperature, and density of the flow could be derived. Details of the flow characterization were discussed previously.[17]

Anthracene was provided by Sigma Aldrich at 99% purity and was used without further purification. It was vaporized upstream of the reservoir in an oven, whose temperature was maintained constant (±2.5 K) by a proportional integrated differential regulator in the 500−550 K range. The vapor pressure of anthracene at the temperature of the oven is modeled by Antoine's law.[17] Then the anthracene vapor is flushed into the nozzle reservoir by a carrier gas flow, at a typical rate of 500 SCCM (SCCM = cubic centimeter per minute at STP), this carrier gas being the same as the buffer gas. The carrier gas flow rate and the pressure in the oven are controlled and adjusted in order to change the anthracene flow rate q_{ant} coming out of the oven. At the temperature of the oven, q_{ant} is determined from the carrier flow rate $q_{carrier}$, the anthracene vapor pressure P_{vap}, and the total pressure in the oven P_{oven} by the relation

$$q_{ant} = q_{carrier} \frac{P_{vap}(T)}{P_{oven} - P_{vap}(T)} \tag{1}$$

To avoid blocking the oven exit and the line by large-sized solid particles of anthracene, the gaseous mixture is filtered by a Swagelock 0.5 mm filter (Swagelok SS-4FWS-05) inside the oven. To avoid condensation downstream of the oven, the gas line between the oven and the reservoir is heated at a higher temperature than the oven, via a 600-W heating wire wound around the tube.

The remaining parts of the experimental apparatus are at room temperature. When the cold supersonic jet meets the surface chamber, which is in front of the nozzle, it becomes subsonic and recovers the initial temperature value, that is, the temperature of the reservoir. Therefore, this surface is cooled by chilled water (15 °C) to maintain a temperature low enough to protect the Viton O-rings. In addition, to avoid too much anthracene penetrating into the pumps, a big cooled collector has been placed between the chamber and the pumps.

The CH radical is produced through the photolysis of Bromoform ($CHBr_3$) introduced in the reservoir. The precursor, liquid at room temperature, is placed in a glass vessel outside the CRESU chamber, and its vapor is entrained by bubbling a small controlled flow of He through it. Photolysis of bromoform is achieved using the fourth harmonic radiation (266 nm) of a Nd:YAG pulsed laser (Spectra Physics, GCR 190, 10 Hz, 20 mJ) propagated along the flow. A sonic expansion of helium through a 10-mm hole is used to avoid anthracene deposition in the photolysis entrance window, which would decrease the photolysis laser energy going into the main chamber. The 266-nm laser radiation produces a stream tube filled with a uniform density of CH radicals. The successive absorption of three photons necessary to dissociate $CHBr_3$ at the wavelength of 266 nm yields a non-negligible fraction of vibrationally excited CH radicals. To ensure full thermalization of the CH radicals (only the ground state is probed), it is therefore necessary to select a carrier gas which efficiently relaxes CH($v > 0$). Earlier kinetic studies[33] have shown that nitrogen (N_2)—in contrast to the commonly used helium gas for instance—meets this requirement. The experimental rate coefficient for the reaction

$$CH(v = 1) + N_2 \rightarrow CH(v = 0) + N_2$$

drops from 10^{-10} cm^3 s^{-1} at 23 K to almost 10^{-11} cm^3 s^{-1} at 584 K. For total number densities in the (2−4) × 10^{16} cm^{-3} range, the corresponding reaction times are ~0.25 and 5 μs for low and high temperatures, respectively. These values remain small compared to the hydrodynamic time of the gas flow (>100 μs). For experiments performed in helium as buffer gas (a flow temperature of 58 K), a small amount of nitrogen (<5%) is added in order to ensure efficient relaxation of the CH($v > 1$).

After formation the CH radicals travel downstream and react with the species present in the flow. Once in the detection region (~200 mm after the nozzle exit), CH radicals are probed by laser-induced fluorescence (LIF) exciting the CH($A^2\Delta$, $v = 0 \leftarrow X^2\Pi$, $v = 0$) transition at 431 nm with a pulsed MOPO tunable laser (Spectra Physics MOPO 730, with frequency doubling option, 10 Hz, ~10 μJ) or a pulsed tunable dye laser (Spectron, 10 Hz, <1 mJ) and monitoring off-resonance fluorescence from the ($A^2\Delta$, $v = 0 \rightarrow X^2\Pi$, $v = 1$) transition at 488 nm. The fluorescence is collected using a fast telescope−mirror combination mounted inside the vacuum chamber and set at right angles to both the flow axis and the probe laser beam. It is then imaged through a slit onto the photocathode of a photomultiplier tube (Thorn EMI, 9813QSB) after passing through a narrow band interference filter centered at 490 nm (band-pass = 10 nm at full width at half maximum, Corion) to reduce the scattered light from the photolysis radiation. PAHs deposition on the mirror and the telescope is avoided by flushing a small amount of helium on the optical surfaces.

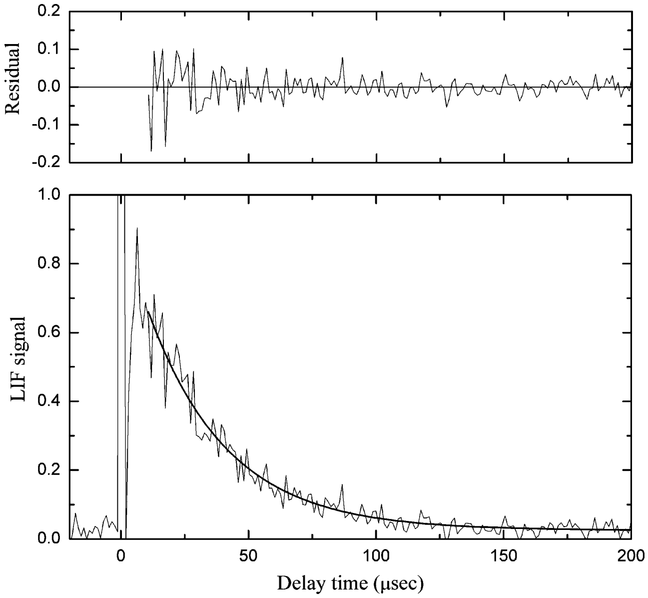


Figure 2. First-order decay of LIF signal from CH in the presence of 47.7 × 10^{12} molec cm^{-3} of anthracene at 119 K in nitrogen, fit to a single-exponential decay, with residuals shown above.

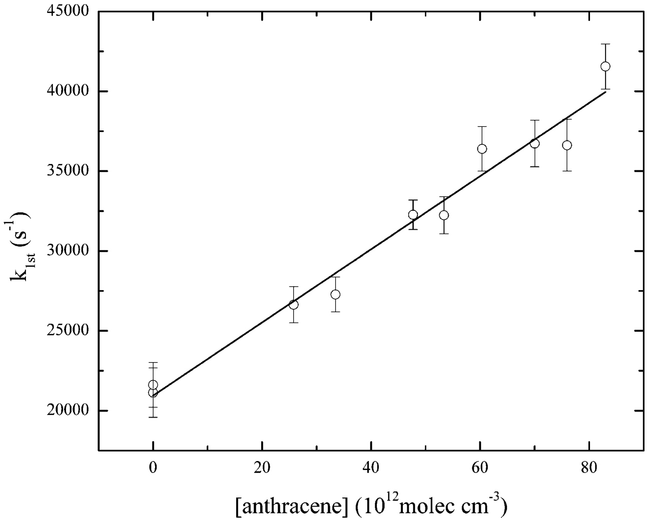


Figure 3. First-order decay constants for CH at 119 K in nitrogen, plotted against the concentration of anthracene.

For a fixed anthracene density (anthracene is always in excess), the LIF signal of the remaining CH radicals is recorded and averaged over several hundreds of laser shots, as a function of the time delay Δt between the photolysis and the probe laser. During this time, CH radicals react with anthracene with a reaction rate constant k. After the CH($v = 1$) relaxation is completed (at least 15 μs), the decrease of the LIF signal as a function of time delay is fitted by an exponential function $\exp(-k_{first}\Delta t)$ using a nonlinear least-squares fitting program employing the Levenberg−Marquadt algorithm (see Figure 2). The measurement was repeated for different anthracene flow rates. Since $k_{first} = k$[anthracene], the plot of k_{first} vs [anthracene] is a straight line whose slope is the rate constant k, at the temperature and density of the nozzle used (Figure 3).

3. Results

Our experimental results are summarized in Table 1 and plot in function of the flow temperature in Figure 4. In the experiments with anthracene, the uncertainty on the rate constant

TABLE 1: Rate Constants for CH + Anthracene Obtained with the CRESU Apparatus

T (K)	carrier gas	total number density (10^{16} molecules cm^{-3})	[anthracene] (10^{12} cm^{-3})	rate coefficient (10^{-11} cm^3 s^{-1})
58	He	4.01	9.6−124.1	13.2
58	He	4.01	10.9−39.8	12.6
58	He/N_2[a] (100:3.2)	4.01	10.9−39.8	13.2
119	N_2	1.96	25.7−83.0	23.5
235	N_2	2.06	14.7−110.2	28.1
470	N_2	2.60	17.6−48.9	41.8

[a] Flow rates: Q_{N2} = 2.7 SLM, Q_{He} = 84.07 SLM.

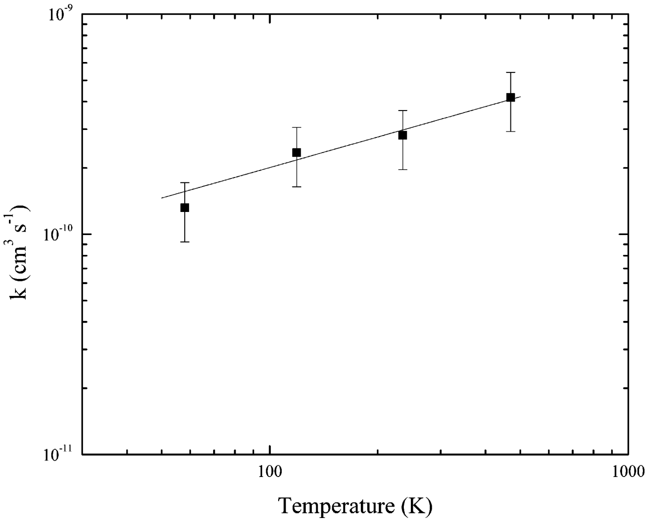


Figure 4. Rate constants for the reaction of CH with anthracene at different temperatures. The circles show the results of the present work, and the line is a fit to our experimental data, yielding $k(T) = (3.32 \pm 1.00) \times 10^{-10}(T/298)^{(0.46\pm0.14)}$ cm^3 molecule^{-1} s^{-1}. Errors bars are shown as 30% of measured rate coefficient as discussed in paragraph 4.

is greater than in previous studies.[34,35] This is because the anthracene density in the flow is more difficult to evaluate than the density of species that are gaseous at room temperature. Because of the oven temperature regulation and gas−liquid equilibrium considerations in the oven, the anthracene density cannot be determined with an uncertainty of less than 15%. We also have to take into account the multiphoton dissociation of anthracene at 266 nm. The laser−molecule interaction can decrease the amount of anthracene in the flow. Experimentally, we have detected CH radicals coming from this photodissociation. But this signal was always at least five times weaker than the signal of CH coming from the photodissociation of bromoform. All together, the uncertainties on the anthracene density added to the statistical uncertainty of the determination of k_{first} lead us to evaluate the uncertainty on the rate constant to be 30%.

As shown in Table 1 and discussed in section 2, the measurement at 58 K has been performed in helium as buffer gas. The introduction of nitrogen in the pure helium flow (~3%) enhances the LIF signal from CH ($v = 0$) in the first 20 μs by almost 30% (Figure 5). The increase is caused by the relaxation of vibrationally excited CH radicals by N_2 molecules from the $v = 1$ to the $v = 0$ energy levels. As discussed above the temporal evolution of the LIF signal is entirely consistent with a very short relaxation time for the excited levels. The rate coefficients measured at 58 K in a pure helium buffer and in a helium/nitrogen mixing are reported in Table 1. The rate constants for the reaction CH($v = 0$) + anthracene obtained with or without nitrogen are similar—within experimental uncertainty. We conclude that the interaction of CH($v = 1$) with anthracene (relaxation or chemical reaction) is not critical for the measurement of the removal rate coefficient of the CH($v = 0$) radical by anthracene. No information on the rate constant of the CH($v = 1$) reaction with anthracene can be inferred from this experiment.

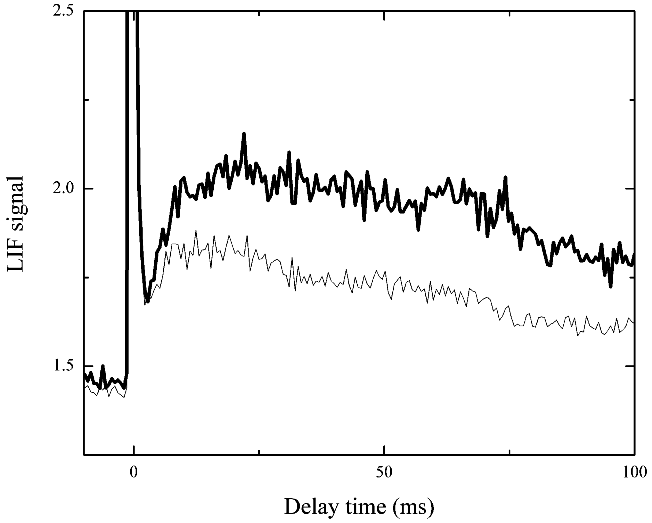


Figure 5. First-order decay of LIF signal from CH in the supersonic flow at 58 K in pure helium (thin line) and in helium with 2% of nitrogen (thick line).

During two experimental runs of experiments at 58 K, the PAH oven temperature was reduced from 515 to 503 K. As a consequence, PAH molecules start to condense rapidly for high saturation ratios. This effect, observed in experiments performed for anthracene at number densities higher than 40 × 10^{12} cm^{-3}, reduces the range of exploitable data points as the real anthracene number density depends then on the unknown number and distribution of anthracene clusters. The solution consists of increasing the PAH oven temperature.

The rate constant increases monotonically as the temperature is increased. This dependence of the rate constant on the temperature can be fitted to the expression $k(T) = (3.32 \pm 1.00) \times 10^{-10}(T/298)^{0.46(\pm0.14)}$ cm^3 molecule^{-1} s^{-1}.

4. Discussion

The experimental results of the present work establish for the first time the kinetics of reaction of CH($v = 0$) with polycyclic aromatic hydrocarbon molecules, starting with anthracene. No direct information about the products of reaction can be inferred from this experiment, and up to now, there are no theoretical studies of the reaction of the CH radical with polycyclic aromatic hydrocarbon molecules. However, mechanistic analysis has been previously performed for reactions of the CH radical with saturated and unsaturated hydrocarbons and with benzene. Canosa et al.[23] have measured the rate coefficient of CH with CH_4 and C_2H_6 between 23 and 300 K. On the basis of their results and on the short lifetime of the CH + CH_4 association complex (C_2H_5, 0.4 ps),[36] they concluded that the reactions of CH with saturated hydrocarbons do not proceed via a collisionally stabilized association complex. Fleurat-Lessard et al.[37] give an indication of the branching ratio for the reaction of CH with CH_4 by measuring the H atom production. These results show only one exit channel which is the formation of C_2H_4 and H atom. More recently, Galland et al.[38] have studied experimentally and theoretically the reaction of CH radical with C_2H_6. They found an H atom branching ratio of 22%. The

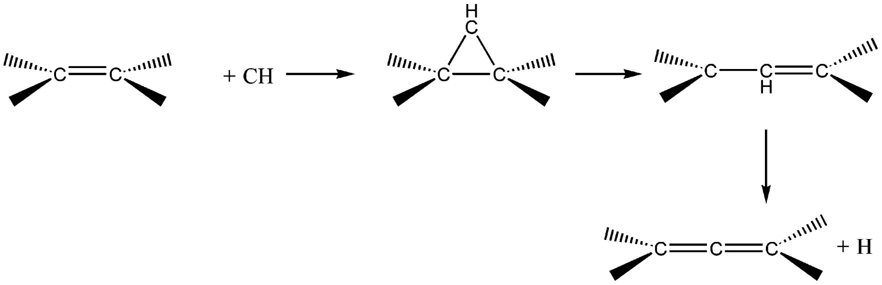


Figure 6. Proposed mechanism for the substitution of an H atom by the CH radical on the double bound of unsaturated hydrocarbons.[36]

calculated potential energy diagram for this reaction at 0 K indicates that the entrance channel is barrierless and leads to the formation of the *n*-propyl radical (n-C_3H_7). Starting from this n-C_3H_7 radical, the three thermodynamically accessible exit channels are the formation of cyclopropane and H atom, propene and H atoms, and ethylene and methyl radical. No reaction path for the C−C insertion of the radical could be found in this ab initio calculation. From these results, they inferred that the CH radical inserts only in CH bond of the C_2H_6 molecule. This mechanism leads, through its minor reaction channel, to the growth of the carbon chain and through its major reaction channel to the formation of ethylene (C_2H_4) and methyl radical (CH_3).

No theoretical calculations have been performed for CH reactions with unsaturated hydrocarbons. However it is established that the products formed by fission of C−C bonds are energetically less favored than in those of CH with saturated hydrocarbons. Canosa et al.[23] and Berman et al.[36] have discussed the possible mechanism of the reaction of CH radical with unsaturated hydrocarbons. The more likely mechanism seems to be the addition of the CH radical on the C=C bond to form a 3-carbon-atom cycle as discussed by Berman et al.[36] and shown in Figure 5.

The general equation for such reaction is

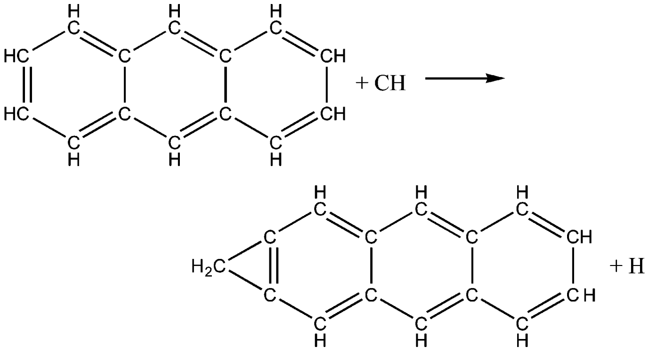
$$CH + C_nH_{2n} \rightarrow C_{n+1}H_{2n} + H$$

These reactions are always exothermic.

In concern of the reaction of CH with aromatic compounds, Berman et al.[36] have measured the rate constant of the reaction of CH with benzene and toluene. They found a rate constant which is close to the gas kinetic rate constant and conclude that the reactivity of CH radical with benzene and toluene is similar to the reactivity of the CH radical with other π-bond-containing species. We can infer from the previous considerations that the main product of the reaction of benzene with CH should be the aromatic compound norcaratriene (C_7H_6). This reaction has an exothermicity of 119.3 kJ·mol^{-1}. In their study of the reaction of the $^3CH_2$ radical with selected polycyclic aromatic hydrocarbons, Kraus et al.[39] assumed that the mechanism of the CH_2 radical reaction with polycyclic aromatic hydrocarbons is analogous to that for benzene. Our measurements of the rate constant of the reaction of CH radical with anthracene is very close to the gas kinetic rate constant and show a positive evolution with the temperature. This behavior is often taken as an indication that the reaction does not involve a collisionally stabilized association process as supposed for the reaction of OH with anthracene.[17] Moreover association processes are expected to be more efficient when the temperature decreases and then would present a maximum if any small energy barrier is present. On the other hand, a large energy barrier would affect the temperature dependence much more significantly than that observed in the present experiment. On the basis of these considerations and on the previous results by Canosa et al.[23] and Berman. et al.,[36] it is consistent to assume that the mechanism of the title reaction proceeds by addition of the radical in the π-system of the molecule followed by an H elimination

$$C_{14}H_{10} + CH \rightarrow C_{15}H_{10} + H$$

However, it is not possible to calculate the exothermicity of the reaction due to the lack of data for the $C_{15}H_{10}$ compound. The main product for the CH reaction with anthracene is expected to be the stable norcaratriene-like compound: cyclopropa[*b*]anthracene.



To confirm the mechanism of this reaction and the formation of cyclopropa[b]anthracene, ab initio calculations are needed.

For this reaction, the kinetic behavior at low temperature is different from that observed for the reaction of CH with linear unsaturated hydrocarbons. Canosa et al.[23] have measured rate constants that increase below room temperature but then appear to reach a limiting value determined by the long-range electrostatic forces between the reagents. Our results show a rate constant that monotonically decreases when the temperature is lowered. This behavior can be due to the presence of a small entrance barrier. But the rate constant of the reaction remains very high even at low temperature and close to the gas kinetic rate constant (i.e., the capture rate).

On the basis of this behavior and in the absence of pressure dependence and product studies, it is difficult to conclude on the true mechanism of the reaction, as pointed out in the review of Troe.[40] The rate constants of fast reactions have been the subject of an enormous amount of theoretical work for more than fifteen years (see the review by Clary[41] or the variety of papers of Troe and co-workers on the subject[42]). The experimental ion−molecule reaction behavior is very well predicted by theory in the 10−300 K temperature range, but it has proven more difficult to reproduce the large variety of temperature dependences observed experimentally for neutral−neutral reactions in the CRESU experiments.[43] Let us just note that the naïve hard sphere model for the present reaction is consistent with the observed temperature behavior and the "size" of the anthracene molecule. To proceed further, it is clearly absolutely necessary to increase the database of reaction rate coefficients for various radicals with polycyclic aromatic hydrocarbons to provide an experimental basis for future theoretical modeling of this class of reactions.

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