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Interaction of gaseous D atoms with CH_3I adsorbed on Pt(111), H/Pt(111), and C/Pt(111) surfaces: From hot-atom to Eley–Rideal phenomenology

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The interaction of gaseous D atoms with methyl iodide molecules adsorbed on Pt(111), hydrogen saturated Pt(111), and graphite monolayer covered Pt(111) surfaces was studied. Direct product rate measurements were employed to determine the reaction kinetics. On all substrates, incoming D atoms abstract the methyl group from adsorbed CH₃I via gaseous CH₃D formation. In the monolayer regime of CH₃I/Pt(111) pure hot-atom phenomenology was observed in the rates. With multilayers as targets, the fluence dependence of the rates get Eley–Rideal-type. With a coadsorbed H monolayer present, the CH₃D rates at a CH₃I monolayer on Pt(111) are affected by the suppression of hot-atom sticking. Accordingly, the rate curves exhibit similar features as expected for Eley–Rideal phenomenology. However, CH₄ as a product and simultaneous abstraction of adsorbed H via gaseous HD and H₂ formation clearly demonstrate that hot-atom reactions occur. With CH₃I adsorbed on a graphite monolayer on Pt(111), the abstraction kinetics of methyl was found to agree with the operation of an Eley–Rideal mechanism. This observation is in line with the expectation that hot atoms do not exist on a C/Pt(111) surface. © *1998 American Institute of Physics*. [S0021-9606(98)01225-2]

I. INTRODUCTION

Reactions between a gas phase atom A and an adsorbed species B are commonly described by two types of mechanisms.

The Eley–Rideal (ER) mechanism¹ infers that a close encounter between A and B leads to a gaseous (or adsorbed) product AB via a direct step:

$$A_{gas} + B_{ad} \rightarrow AB_{gas} \quad \text{or} \quad AB_{ad}. \tag{1}$$

In the hot-atom or hot precursor mechanism,² the one-step reaction (1) is replaced by a two-step reaction through the introduction of an intermediate hot-atom species A^* , which is not accommodated at the surface but keeps the energy gained in the adsorption well:

$$A_{gas} \rightarrow A^*, \tag{2}$$

$$A^* + B_{ad} \rightarrow AB_{gas}$$
 or AB_{ad} . (3)

As the hot atom A^* is not accommodated on the surface, the reaction energy set free by the formation of AB is available to the product, and if this energy is not dissipated into the substrate, the product desorbs. If this is not the case, the product might desorb thermally if the substrate temperature is high enough. The further discussion will be restricted to those cases which lead to a gaseous product AB_{gas}.

Provided that the atom/adsorbate reaction is carried out in such a way that a flux Φ of A atoms is directed at t=0 at a surface with B coverage $(B)_0$ and kept constant at later times, according to the ER reaction scheme the rate of formation of the product AB_{gas} should vary as

$$d(AB_{gas})/dt = \sigma \Phi(B)_0 \exp(-\sigma \Phi t), \qquad (4)$$

with σ as a reactive cross section. Due to the locality of the reactive events, σ should be in the order of molecule dimensions, i.e., in the order of Å².

Recently, studies were performed using direct product rate measurements during reactions between gaseous H (D) atoms and D (H) adsorbed on Ni and Pt surfaces.^{3–5} The measured kinetics of HD formation was found to be at variance with the ER rate of the AB_{gas} product, as expressed in Eq. (4). Furthermore, homonuclear reaction products like D₂ in H \rightarrow D_{ad} reactions were observed,^{6,3–5} which are unexpected in the framework of the ER mechanism.

A more appropriate explanation of the experimental results was obtained with the assumption that hot-atom processes govern the atom/adsorbate reaction pathways. The fact that in addition to HD, homonuclear products D_2 and H_2 were observed as reaction products in $H \rightarrow D_{ad}$, respectively, $D \rightarrow H_{ad}$ reactions, lead to the proposal of hot-atom generation upon the impact of the gaseous atom at a D covered surface:

$$H+D_{ad} \rightarrow H^*+D_{ad}$$
 or D^*+H_{ad} . (5)

Gaseous products then are formed by reactions between hot H^* (D*) atoms and adsorbed D atoms according to the following scheme:

$$H^* + D_{ad} \rightarrow HD_{gas}, \tag{6}$$

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$$\mathbf{D}^* + \mathbf{D}_{ad} \rightarrow \mathbf{D}_{2.gas}. \tag{7}$$

The introduction of sticking of the hot-atom species H^* and D^* provides a process which is competitive to reaction:

$$H^* + X \rightarrow H_{ad}$$
 and $D^* + X \rightarrow D_{ad}$, (8)

with X denoting an empty site on the surface. If the probabilities of reactions of hot atoms through steps (6) and (7) are smaller than the probability of hot-atom sticking, step (8), an efficient means is supplied for the deactivation of hot atoms on surfaces which exhibit empty sites. This explains why the abstraction of D (H) from Ni(100),³ Pt(111),⁴ and Pt(110)⁵ is inefficient at small total coverages (Θ_D plus Θ_H), but becomes more efficient at a higher total coverage.

Further experimental evidence for hot-atom-based processes was provided by the observation that upon interaction of H atoms with mixed D/CD_3I adlayers on Ni(100) surfaces, gas phase CD_4 species were formed in addition to CD_3H product molecules.⁷ As an origin of these latter product molecules, the reaction step sequence,

 $H+D_{ad}\rightarrow D^*+H_{ad}$, $D^*+CD_3I\rightarrow CD_4+I_{ad}$,

was proposed, fully in line with the hot-atom scheme described above.

Recent molecular dynamics calculations of the interaction of H with $H_{ad}/Si(110)^8$ and $H_{ad}/Cu(111)^9$ revealed reactive trajectories which must be addressed as of the hotatom type.

The present study was performed in order to investigate whether hot-atom processes generally dominate atom/ adsorbate reactions. The idea was to compare reactions between D atoms and CH_3I adsorbed in several environments: monolayer, multilayer, metallic surface, passivated surface. It was expected that through changes in the nature of the substrate and reactant environment hot-atom generation and deexcitation, processes (5) and (8), could be manipulated in such a way that the kinetics of gas phase product formation would be affected.

Methyl iodide was chosen as the adsorbed reactant molecule because monolayers as well as multilayers of CH_3I can be easily prepared on various substrates. Furthermore, it is known that CH_3I reacts with H atoms toward methane,^{7,10} which can be identified reliably through its mass spectrometer fragmentation pattern.

II. EXPERIMENT

The experiments were carried out in a UHV system equipped with instrumentation for low-energy diffraction (LEED), Auger electron spectroscopy (AES), and thermal desorption spectroscopy (TDS). The sample, a Pt(111) single crystal, was mounted between two Ta wires which were clamped to two Cu rods connected through sapphire spacers to the bottom of a small cryostat. Sample temperatures between 85 and 1300 K could be maintained and regulated through Ohmic heating and LN_2 cooling. The atom source was built according to a published design.¹¹ It consists of a 50 mm long W tube, which is heated at its front end, 1950 K in the present study, as determined by pyrometric measurements. Through the cold back end of the tube, H₂ or D₂ gas is supplied from a pumped gas manifold. The atom source is located in a small, differentially pumped cylindrical vacuum chamber (source chamber) attached to the main system. The front end of the source chamber has an aperture of 9 mm diam which can be closed by a mechanical shutter. A computer-controlled quadrupole mass spectrometer (QMS) is located in the source chamber.

For thermal desorption (TD) measurements, the sample was placed in front of the open aperture and a digitally controlled linear temperature ramp was applied to the sample. Partial pressures of relevant species, including their fragmentation products, were monitored through multiplexing the QMS.

Reaction measurements were performed at 85 K with adsorbed layers which were prepared according to the results of the TD measurements. The sample with a wellcharacterized adlayer coverage was placed in front of the closed aperture. The atom source was operated and after stabilization of tube temperature and gas flow through the tube, the shutter was opened while monitoring mass spectrometer signals at preselected amu values. At reaction completion the shutter was closed and TD spectra were measured to determine the nature and quantity of adsorbed species after reaction. The configuration represents a pumped reactor and the quadrupole signals are therefore proportional to the rates of product formation.

The atom fluxes used were calculated from the gas flow through and the front temperature of the W tube. These fluxes are given below in units of monolayers per second, Ml s⁻¹. According to the atom density of the Pt(111) surface, $1 \text{ Ml}=1.5\times10^{15} \text{ atoms/cm}^2$.

Graphite covered C/Pt(111) surfaces were prepared by annealing a clean sample in 5×10^{-5} Torr ethane atmosphere at 1000 K. It has been shown that this procedure leads to the generation of graphite islands on a Pt(111) surface.¹² A comparison of the desorbed amounts of H₂ after dosing 1000 L molecular hydrogen to Pt(111) and C/Pt(111) revealed that only a few percent of the Pt(111) surface was not covered by C after four annealing cycles in ethane. Graphite islands on Pt(111) surfaces are stable toward D atom exposure.¹³

Methyl iodide exposures in $L=10^{-6}$ Torr s are not corrected for ionization efficiency because the related factor is not known. Reaction rates are given below in arbitrary units. Since methyl iodide exhibits a constant sticking coefficient throughout the coverage range investigated here, and methyl abstraction is complete, integration of the rate curves can be used to deduce the rates in Ml s⁻¹ units.

III. RESULTS

A. Preparation of CH₃I adlayers

The surface chemistry of methyl iodide on Pt(111) surfaces was investigated in the past by several researchers.¹⁴ Our TD spectroscopy results completely agree with what was reported previously, however, the exposure needed to establish the monolayer on Pt(111) with a coverage of 0.2 was *ca*. 25 L instead of *ca*. 5 L in previous work. On Pt(111), CH₃I adsorbs molecularly at 85 K, only above 210 K decomposi-

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FIG. 1. Rates of gaseous CH₃D (17 amu) formation measured during directing a D atom flux of 0.15Ml s⁻¹ at CH₃I covered Pt(111) surfaces at 85 K. The atom flux was started at t=0. The CH₃I exposures noted on the right are stacked as the rate curves on the left. The CH₃I monolayer corresponding to

tion of monolayer CH₃I was observed in accordance with the literature. On H/Pt(111) and C/Pt(111) surfaces CH₃I adsorbs and desorbs exclusively molecularly.

B. Reaction measurements $D \rightarrow CH_3 I/Pt(111)$

a coverage of 0.2 was achieved after 25 L CH₃I exposure.

D atoms abstract the methyl group from methyl iodide adsorbed on Pt(111) surfaces, as was previously observed on Cu(100)¹⁰ and Ni(100)⁷ surfaces. The rates of the CH₃D reaction product measured in the monolayer and multilayer regimes of CH₃I are reproduced in Fig. 1 through the 17 amu signals. In the monolayer regime, at the reaction start (the opening of the shutter), the methane rates jump to small values, increase by small amounts in the early reaction period, and exhibit a sharp rise after the D atom fluence has reached *ca*. 1.5 Ml. Rate maxima occur after a fluence of *ca*. 3 Ml D atoms, followed by exponential decay. Logarithmic plots of the rates in the late reaction period reveal σ =0.9 Å² as a reaction cross section.

In the multilayer regime, CH₃I exposures above 25 L, the kinetic features in the early reaction period change significantly. The initial rates jump to higher values and the rates increase toward its maximum is faster. At the highest methyl iodide coverage the rate jumps to its maximum right at the reaction start, followed by a close to exponential decay. A logarithmic plot of the rate reveals $\sigma=0.4$ Å² in the late reaction period for the 300 L rate curve.

The yield toward CH₃D obtained from integrated rate curves was found strictly proportional to the CH₃I coverage



FIG. 2. Mass spectrometer signals of relevant species measured during directing a D atom flux of 0.15 Ml s^{-1} at Pt(111) surfaces which were covered with a CH₃I monolayer (dotted lines) or covered with a saturated H layer and a CH₃I monolayer (full lines). Adsorption and reaction temperature was 85 K. The atom flux was started at t=0.

deduced from TD spectra. This applies to the monolayer as well as to the multilayer regime.

A detailed view on the relevant signals measured during the reaction of methyl iodide monolayers with D atoms is shown by the dotted lines in Fig. 2. The relative amplitudes of the 17, 16, and 15 amu signals correspond to the fragmentation pattern of CH₃D, which is available from tabulated data.¹⁵ Negligible signals of H₂ and HD confirm that the abstraction of the methyl group from methyl iodide is the only reaction that occurs between D and CH₃I.

C. Reaction measurements $D \rightarrow CH_3 I/H/Pt(111)$

In order to investigate the effect of a coadsorbate on the reaction kinetics, monolayers of CH₃I were prepared on Pt(111) surfaces which were already saturated with hydrogen by exposure of 1000 L molecular hydrogen. Relevant mass spectrometer signals measured during the reaction with mixed H/CH₃I adlayers are shown as full lines in Fig. 2. At the reaction start, the 17 amu signal jumps to a value which is significantly bigger than that obtained without coadsorbed H. Within a fraction of a monolayer of D fluence, it assumes its maximum. The late rate decay is an exponential and is characterized by the cross section σ =0.8 Å².

If CH_3D were the only product, the 17, 16, and 15 amu signals (full lines) in Fig. 2 should be proportional to each other and exhibit the correct fragmentation pattern amplitudes. This pattern is illustrated by the amplitudes of the 17, 16, and 15 amu signals measured during the reaction of D with a CH_3I monolayer, as shown by the dotted lines in Fig. 2. The fact that the (full line) 16 and 15 amu signals are higher than they should be for a CH₃D product, suggests the formation of an additional product. Since no 18 amu signal was detected, contributions to the 16 and 15 amu signals can only stem from CH₄. Using the 17 amu signal and the fragmentation factors, the CH₃D contributions to the 16 and 15 amu signals were removed in order to isolate the additional product. CH₄ was confirmed as this product by its 16, 15, and 14 (not shown) amu fragmentation pattern.¹⁵ Accordingly, with the coadsorbed H adlayer present on the surface, in addition to CH₃D a CH₄ product is formed upon reaction. In the above-mentioned study on reactions of H atoms with mixed D/CD₃I adlayers on Ni(100) surfaces,⁷ an analogous product, CD₄, was observed.

From the decay of the CH₄ signal, available after separation of CH₃D and CH₄ components in the 16 amu signal of Fig. 2, a cross section for CH₄ formation of σ =3.3 Å² was obtained.

As expected, the coadsorbed H species gets abstracted toward HD and H₂, documented by the 3 and 2 amu signals in Fig. 2. Both signals jump at the reaction start to values that are close to their maxima. The late rate decay for both products is exponential, faster for H₂ than for HD, and corresponds to cross sections of 3.5 and 1.7 Å². The similarity of the CH₄ and H₂ cross sections suggests that these products occur through related processes. Analogous behavior was observed in the study on reactions of H with mixed D/CD₃I adlayers on Ni(100) surfaces.⁷

D. Reaction measurements $D \rightarrow CH_3 I/C/Pt(111)$

D atoms directed at adsorbed CH₃I in the monolayer and multilayer regimes on C/Pt(111) result in the formation of CH₃D as the only gaseous product. The 17 amu rate curves shown in Fig. 3 are therefore sufficient for the demonstration of the kinetics. In the monolayer regime, even at the smallest coverage (5 L methyl iodide exposure), the CH₃D rates jump at the reaction start to their maximum values, followed by an exponential decay. The same behavior is seen in the multilayer regime. For illustration of the reproducibility of the rate measurements, a multilayer (300 L) rate curve from Fig. 1 is included as a dotted line in Fig. 3. With methyl iodide multilayers on Pt(111) and on C/Pt(111), the CH₃D rates should exhibit identical characteristics at the same coverage, and this is confirmed by the data. A logarithmic plot of the 600 L rate curve in Fig. 3 is not linear, and a meaningful constant cross section for the thickest multilayer cannot be deduced. The other rate curves, measured at smaller coverages, allow us to specify a reaction cross section of σ $= 0.7 \text{ Å}^2.$

IV. DISCUSSION

The interaction of D atoms with CH_3I adsorbed molecularly in various environments, monolayer, multilayer, with and without coadsorbed H on a Pt(111) surface, and on a graphite monolayer on Pt(111) leads to CH_3D formation. This is in accordance with previous investigations in which a methane reaction product was observed in the interaction of H (D) with methyl iodide adsorbed on $Cu(100)^{10}$ and



FIG. 3. Rates of gaseous CH₃D (17 amu) formation measured during directing a D atom flux of 0.15 Ml s⁻¹ at CH₃I adlayers on a graphite monolayer covered Pt(111) surface at 85 K. The atom flux was started at t=0. The CH₃I exposures noted on the right are stacked as the rate curves on the left. The CH₃I monolayer corresponding to a coverage of 0.2 (with respect to the Pt(111) atom density) was achieved after 25 L CH₃I exposure.

 $Ni(100)^7$ surfaces. Reactions of D with mixed H/CH₃D monolayers on Pt(111), in addition, lead to CH₄, HD, and H₂ as gaseous products. Equivalent products were measured in the study on D/CD₃I adlayers on Ni(100).⁷ Accordingly, the present data are consistent with published results.

The reaction between D atoms and CH_3I is exothermic and should not exhibit a significant barrier. If there is one, the thermal energy of atoms from a heated source, typically 0.2 eV as the most probable energy in a Maxwellian distribution, should suffice to overcome the barrier.

No other gas phase reaction products were observed. HI was looked for, but none was detected. That I remained at the surface was suggested by the observation that the capacity of a Pt(111) surface for hydrogen adsorption was substantially reduced after completed reaction between D and adsorbed CH_3I . In order to restore a clean surface, flashing the sample above the I desorption temperature of 800 K was therefore routinely performed prior to preparation of the reactant adlayers.

The amount of methane products formed until reaction completion was found to be strictly linearly related to the methyl iodide coverage prior to the reaction at all surfaces, Pt(111), H/Pt(111), and C/Pt(111), in the monolayer and multilayer regimes. It is therefore safe to assume that the reactions consumed all methyl groups available on the surface.

Control experiments with an unheated atom source and otherwise unchanged experimental conditions, i.e., with H_2

instead of H directed at CH_3I adlayers, showed no gaseous reaction products, which is expected at an 85 K substrate temperature.

Restricting at first to the $CH_{3}I/Pt(111)$ and CH₃I/H/Pt(111) systems, the measured reaction kinetics data will be analyzed within the following framework. An incoming D atom is assumed to stick with probability p_s if its impact on the Pt surface occurs at an empty site. Alternatively, it is transformed into the hot-atom D* state. At sites occupied with H or D or methyl iodide, it either becomes a hot D* atom or generates a hot H* or D* atom with specific probabilities. Hot D* (H*) atoms travel across the surface, and in collisive encounters with adsorbed CH₃I they abstract methyl to form CH_3D (CH_4) with a probability p_r . At the given temperature of 85 K, methane products desorb immediately and I remains on the surface. Upon encounter with an empty surface site, hot atoms stick with a probability p_{hs} . In the further discussion it is assumed that the probabilities p_s and p_{hs} are bigger than p_r .

The repulsive interaction between methyl iodide molecules adsorbed on Pt(111) causes the monolayer coverage to be only about 0.2. This leaves many empty sites for D adsorption and D* sticking, if D atoms impinge at a submonolayer or monolayer CH₃I covered surface. Accordingly, there is a considerable chance for hot D* atoms to stick at these sites while moving on the surface. The assumption $p_{hs} > p_r$ makes sticking of hot atoms a very efficient step competitive to reactive events. As long as a surface exhibits empty sites, this competing step will lower the rate of methane formation significantly below that value which would be achieved without hot-atom sticking.

The action of this scenario is seen in the kinetics measured in the monolayer CH₃I/Pt(111) regime, as depicted in Figs. 1 and 2 (dotted lines). The rate jumps are small because the probability p_r is small and there are many empty sites available on the surface. The rates stay small as long as the surface is not fully covered, which corresponds to the early reaction period. Only after the surface is completely covered with D and CH₃I through adsorption of D from the gas phase or through sticking of D* species, the methane rate starts to grow substantially. This situation is met after a fluence of *ca*. 1.5 Ml D. In this early reaction period, the rate of methane formation strongly contradicts the operation of an ER mechanism, since the methane rate increases although the CH₃I concentration on the surface decreases. Beyond the reaction rate maximum, in the late reaction period, the total coverage, given by the fractional coverages of CH₃I and D, has assumed saturation. Stationary conditions with respect to the total coverage are maintained under a continuous D flux. Accordingly, no or almost no empty sites are present on the surface in the late reaction period, and hot-atom sticking is suppressed. Each hot D* atom has to react eventually with an adsorbed methyl iodide toward CH₃D or an adsorbed D toward D₂. Since the amount of CH₃I on the surface is limited, blocking of competitive hot-atom sticking in the late reaction period causes the CH₃D rates to decrease exponentially. In this late reaction regime, the phenomenology of hot-atom processes necessarily lead to an ER-like exponential dependence between rate and time (atom fluence). A conclusion on the operating mechanism is, however, not possible from that phenomenological feature. Neither HD not H_2 are expected as products from reactions between D and adsorbed CH_3I if D^*-CH_3I encounters do not cause the dissociation of CH_3I . This is confirmed in Fig. 2 (dotted lines).

It is important to realize that in an experimental setup for the measurement of product rates which does not allow us to monitor the initial reaction region or does not provide a strict separation between the sample and the atom source prior to the reaction start, the outcome of a reaction kinetics measurement would confirm the ER reaction scheme, as only kinetic data from the late reaction period would be available.

The essential input for rationalizing the measured kinetics in the early reaction period is given by the competition between the sticking and reaction of hot atoms. In the CH₃I multilayer regime the hot-atom picture does not apply since a multilayer does not provide a deep adsorption well for incoming D atoms which supplies potential energy to the atom.² However, D atoms are small particles and can migrate through a not very dense layer of stacked molecules. The rate of CH₃D formation should become proportional to the concentration of CH₃I molecules available for a reaction in the target, and, accordingly, the rate step in the multilayer regime should be proportional to the CH₃I coverage. This was observed experimentally. Necessarily, the reaction kinetics assumes ER phenomenology, i.e., the rates strictly follow an exponential decay law. The experimentally determined reaction cross section is smaller than for the hot-atom case in the monolayer regime, $\sigma = 0.4 \text{ Å}^2$, as compared to $\sigma = 0.9 \text{ Å}^2$. The small reaction cross section implies that a considerable fraction of the incoming D atoms do not react.

The reaction yield in the limit of infinite thickness of the adsorbed methyl iodide layers, available through the time-integrated CH_3D signal and the accumulated D flux, was not measured. However, even with the top rate curve in Fig. 1 the height of the initial rate jump indicates that only every sixth incoming D atom reacted. The reflection of atoms might be a non-negligible process.

A comparison of the rates measured at adsorbed CH₃I and coadsorbed H and CH₃I, full and dotted lines in Fig. 2, is illustrative concerning the action of coadsorbed H on the kinetics of CH₃D formation. On Pt(111) surfaces, covered with H at saturation, sticking of hot atoms is suppressed to a great extent. Sticking is not completely excluded because a H saturation coverage of only about 0.7 is achieved through dosing of molecular H₂ to Pt(111) surfaces.¹⁶ Therefore, not all sites at the Pt(111) surface are blocked by adsorbed H. However, the 17 amu full line rate curve in Fig. 2 illustrates that the reduction of the number of sites available for hotatom sticking has a significant effect on the CH₃D rate in the early reaction period. The rate jump becomes bigger and the atom fluence necessary to achieve the rate maximum is reduced. Both phenomena are expected within the present framework.

The presence of the coadsorbed H adlayer has additional consequences which are easy to understand within the current scenario. Incoming D atoms produce hot H^* atoms which can react with adsorbed H to form H_2 . These molecules are monitored in the 2 amu signal in Fig. 2. Further-

more, HD becomes a significant abstraction reaction product, either through D^*-H_{ad} collisions or through H^*-D_{ad} collisions and the subsequent reaction. As the hot-atom species, H^* can also react with adsorbed CH_3I to form CH_4 , the 16 and 15 amu signals in Fig. 2 (full lines) contain the QMS fragmentation species from the most abundant product, CH_3D , and a smaller contribution from CH_4 . The cross sections for the products which are generated by hot H^* , H_2 , and CH_4 , should be similar. This is confirmed and gives further support for the assumptions that hot H^* atoms are the source of both products.

The products and reaction kinetics measured during the reaction of D with CH_3I adsorbed on Pt(111) and H/Pt(111) can be interpreted in a consistent way, based on a hot-atom scenario. The essential assumption for the explanation of the rates at the reaction start and in the early period is the competition between sticking and reaction of hot atoms, expressed by probabilities which favor sticking, provided that empty surface sites are available. This competition has significant, but easy to understand consequences for the kinetics discussed above. The experimental data in the early reaction period support the assumptions made on the relative probabilities of sticking and reaction. Furthermore, the consequences of the proposed hot-atom generation pathways are confirmed by experiment through reaction products like CH_4 and H_2 in reactions of D with H/CH₃I adlayers.

The CH₃D rates measured during interaction of D with submonolayers or a monolayer of CH₃I adsorbed on C/ Pt(111), as shown in the bottom part of Fig. 3, exhibit a perfect ER phenomenology. At start of the D atom flux, the CH₃D rates jump to their maximum values and decay exponentially at later times. This behavior in the early reaction period contradicts the operation of a hot-atom mechanism, since many empty surface sites are available on the C/ Pt(111) surface, even at a monolayer coverage of CH₃I. In view of the present assumptions, sticking of hot atoms should therefore cause small initial CH₃D rates, as was observed with Pt(111) surfaces.

In previous investigations it was shown that a C layer on Pt lifts the metallic character of the substrate. A comparison of adsorption properties of benzene revealed that on a graphite monolayer on Pt(111) surfaces benzene physisorbs, contrasting chemisorption on Pt(111).¹⁷ Furthermore, a study of the interaction of H atoms with C/Pt(110) surfaces demonstrated that H atoms are bound only at the edges of the graphite islands via CH and CH₂¹⁸ group formation. Leaving these edge effects aside, it is therefore safe to assume that H (D) atoms do not adsorb on a graphite monolayer. On the basal plane of graphite, hot-atom sticking therefore can be excluded. A hot D* atom, generated upon impact of D on the C/Pt(111) surface, will move across the surface until it eventually reacts with an adsorbed CH₃I. With this restriction, at the small D atom fluxes applied in the present measurements, a hot-atom scenario predicts a CH₃D rate which is constant as long as CH₃I is available on the surface for reaction and decays abruptly if all methyl is consumed. The experimentally observed kinetics contradicts this.

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trolled by an ER mechanism, but is controlled by ER. The question can be put another way: do hot atoms exist at all on a graphite monolayer on Pt(111)?

The generation of hot D* atoms requires a strong attractive potential between incoming D and the substrate.² Such a strong adsorption potential well does not exist in the D–C/ Pt(111) interaction, unlike to the D–Pt(111) interaction, where this well has a depth of about 2.5 eV. It is therefore plausible to assume that a hot-atom state on C/Pt(111) does not exist. Upon collision with the methyl iodide covered C/ Pt(111) surface, D atoms either are reflected, or abstract the methyl group from the methyl iodide molecule within the reaction range specified by the cross section. This is the scenario underlying the classical ER mechanism and, accordingly, the ER rate kinetics is seen in Fig. 3. Through the action of the graphite monolayer, the kinetics of methyl abstraction from adsorbed CH₃I by D atoms is switched from a hot-atom scenario to an ER scenario.

The kinetics of CH_3D formation in the CH_3I multilayer regime on C/Pt(111) surfaces, illustrated by the rate curves in the top part of Fig. 3, does not exhibit features different from those observed with multilayers on Pt(111), as expected.

Finally, the reflection of incoming atoms is addressed. Irrespective of the actual mechanism, even at the CH_3D rate maxima, the measured rates were only about a few percent of a monolayer per second, although the atom flux was more than ten percent of a monolayer per second. This suggests that a non-negligible fraction of incoming atoms exhibit trajectories which lead to reflection. This point needs clarification.

V. CONCLUSIONS

The interaction of gaseous D atoms with adsorbed CH_3I molecules was studied in the monolayer and multilayer regimes on Pt(111), on hydrogen covered Pt(111), and on graphite monolayer covered Pt(111) surfaces. The reaction product is CH_3D formed by abstraction of the methyl group from the methyl iodide molecule.

The kinetics of reactions of D with monolayer CH₃I on Pt(111) are controlled by a hot-atom mechanism, with a fluence dependence of the CH₃D rate which illustrates the competition between a hot-atom reaction and hot-atom sticking at empty surface sites. The reaction cross section is $\sigma = 0.9 \text{ Å}^2$.

Reactions of D with multilayer CH₃I exhibit CH₃D rates which are in line with the operation of an Eley–Rideal-type mechanism. The transition from the monolayer to the multilayer regime is illustrated in the rates. The multilayer CH₃D reaction cross section is $\sigma = 0.4$ Å².

The kinetics of reactions of D with a monolayer of CH_3I coadsorbed with a saturated H layer on Pt(111) is controlled by a hot-atom mechanism, and the influence of site blocking for hot-atom sticking is apparent in the rates. The formation of hot H* atoms through collisions of D with the substrate leads to a small contribution of CH_4 in the reaction products. The CH_3D reaction cross section is $\sigma = 0.8$ Å².

Reactions of D with CH_3I adsorbed on a graphite monolayer on Pt(111) reveal a CH_3D formation kinetics which is

This suggests the question of whether the reaction of D with methyl iodide on C/Pt(111) not only looks like conThe action of the C layer on Pt(111) consists in a suppression of the metallic character of the substrate, thereby altering the kinetics from the hot-atom to the Eley-Rideal type. The results confirm the expectation that hot-atom reactions between gaseous D atoms and an adsorbate require a strong adsorption well (e.g., metallic substrate) in the D– substrate interaction. A weak D–substrate interaction (e.g., in-plane covalent substrate) leads to reaction mechanisms which are compatible with the Eley–Rideal reaction scheme.

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