

A "CHOPPED FAST FLOW" TECHNIQUE FOR TRANSIENT SURFACE REACTION RATE MEASUREMENT: CARBON DEPOSITION AND OXIDATION ON HOT Pt

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ABSTRACT

A novel "chopped fast flow" technique for surface reaction studies is described. It extends the molecular beam chopping approach to fast flow systems, exploits higher reactant and product fluxes, and permits transient rate measurements of fast surface reactions at much higher pressure. It employs an oscillating needle gas source to generate reactant square wave flows. The method was used to measure rates of carbon deposition following impact of hydrocarbon molecules on a hot Pt surface ($T > 1000^\circ\text{K}$). Square wave flows of hydrocarbon and oxygen, out of phase, produced period changes in carbon coverage, surface work function, and thermionic electron emission current. Carbon deposition rates were inferred from the variation of emission current with time. Deposition probabilities were low and very sensitive to hydrocarbon chain length. The results suggest that energy transfer during the short physisorption lifetime of the hydrocarbon molecule limits the deposition probability.

KEY WORDS

Chopped fast flow; transient rate measurements; hydrocarbon decomposition on surface; oscillating needle gas source.

INTRODUCTION

Reactant flux chopping is a useful strategy for measuring heterogeneous reaction rates under molecular beam conditions (Schwarz and Madix, 1974). The surface is exposed to a modulated reactant flow, and the response of a product flux or surface coverage is recorded. The reaction rate is inferred either from the instantaneous response or from an average response versus chopping frequency.

We show here that the same strategy can be experimentally realized even when the mean free path is small, as in a fast flowing gas at one torr. We describe a novel oscillating gas source that achieves this modulation or "chopped fast flow" capability. We then report on its use in measuring the rate of increase of carbon coverage when hydrocarbon molecules decompose on a hot Pt surface.

Reactant flux chopping at high rather than low pressures has several advantages. Since the reactant fluxes can be many orders of magnitude higher than in a molecular beam, product detection is simplified. Some phenomena, such as film growth and bulk solution, may occur more readily at high pressure.

Carbon deposition on a hot surface is a subject of intrinsic interest on several grounds, as well as a convenient test case for the chopped fast flow technique. In heterogeneous catalysis, mono- and multi-layers of carbon are thought to influence the activity and selectivity of noble metal catalysts (Somorjai and Zaera, 1982). The growth of soot in flames involves carbon deposition following impact and decomposition of organic molecules on a hot carbon surface (Harris, 1984).

Hydrocarbon decomposition has several implications for the study of energy transfer at surfaces. Hydrocarbons adsorb intact on Pt, and chemisorption, which must precede carbon deposition, requires an activation energy (Somorjai, 1977). At high temperatures energy transfer from the metal must compete with rapid desorption, so that the rate of change of carbon coverage is a qualitative measure of the efficiency of energy transfer.

Carbon deposition is relevant to the study of oscillating reactions. Under some conditions the deposition/oxidation of carbon on hot Pt in a steady flow of both hydrocarbon and oxygen is oscillatory (Halpern and co-workers, 1983; Gross and Halpern, in preparation). The maximum frequency observed was 15 Hz, higher than that reported for any other surface reaction. In order to clarify the mechanism of this oscillation, it is necessary to know the rates of deposition and oxidation.

Finally, it is experimentally simple to detect carbon deposition on a hot metal, even at high pressure, by monitoring thermionic electron emission (Halpern, al Mutaz, and Douyon, 1981). The emission current j varies with temperature and work function ϕ according to the equation

$$j \propto \exp(-\phi/kT) \quad (1)$$

Emission from noble metals is increased one thousandfold by a monolayer of carbon. Even at a pressure of one torr, thermionic emission provides an instantaneous and sensitive means of observing small changes in carbon coverage. When coupled with the chopped fast flow technique, thermionic emission permits measurement of the deposition rate from the emission current response to square pulses of hydrocarbon reactant.

EXPERIMENTAL TECHNIQUE

Chopped fast flow experiments were carried out in a glass, low pressure fast flow system typically operated at pressures of .5 torr and flow speeds of 5000cm/sec. The system had two key assemblies: a) A thermionic diode reactor containing a noble metal filament, and b) One or more oscillating needle gas sources which permit reactant flux chopping.

Thermionic Diode Assembly

The diode reactor contained an electrically heatable noble metal filament (.0127 cm diameter, 2 cm length) mounted on a brass and ceramic frame (Halpern, al Mutaz, and Douyon, 1981). The filament served as the catalyst surface and electron emitter. A nickel wire electron collector was positioned 3 mm from the filament. Collector voltage was supplied by a 9 volt battery and emission currents were measured with a Keithley 602 electrometer having a frequency response of 0 - 40 kHz.

A .0025 cm diameter Pt/Pt-10% Rh thermocouple was spotwelded to the center of the filament. A thermocouple is more convenient for temperature measurement than resistance taps, but if the filament is heated by direct current, the thermocouple voltage will be falsified. Therefore the filament was heated with alternating current. The filament thermal response in flowing gas smoothed out the small 60 cycle Joule heating variations, and the correct D.C. thermocouple voltage was registered on a chart recorder or digital multimeter.

Oscillating Needle Gas Source

The hot filament was exposed to square wave fluxes of hydrocarbon and oxygen in a steady stream of inert carrier gas. The hydrocarbon and oxygen fluxes were timed to arrive at the filament out of phase. Each reactant square wave was generated in an oscillating needle gas source as shown in Fig. 1.

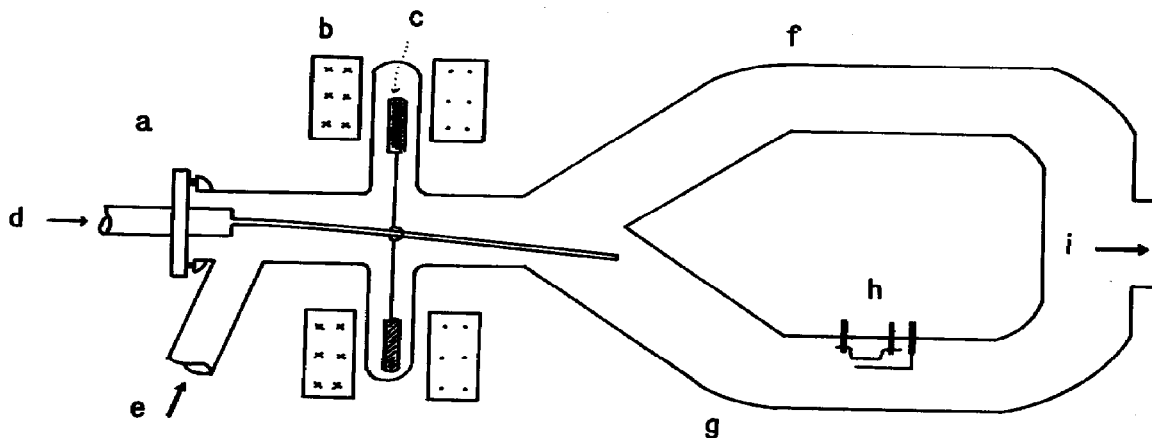


Fig. 1. Oscillating needle gas source; a) needle assembly; b) coil; c) iron slug; d) reactant inlet; e) carrier inlet; f) bypass path; g) experiment path; h) thermionic diode; i) to pumps.

The oscillating needle gas source consisted of a flexible, magnetically activated hypodermic needle tube which directed the reactant either toward the filament or away from it. The guidance was achieved by splitting the main flow into two branches as shown in Fig. 1. One branch contained the Pt filament assembly, while the other branch bypassed the filament and led to the pump. The needle flow oscillated between these two branches, injecting reactant alternately into each branch. The needle tip swept close to a "razor blade" partition which served to demarcate the branches and guarantee initially sharp edges to the square pulse. The filament was in this way exposed to a square wave of the reactant.

One needle assembly and its magnetic drive is shown in Fig. 1. The needle was coupled to a wire crossbar bearing magnetic slugs at each end. These slugs were pulled into coils that were alternately energized and de-energized by an oscillator circuit. This mechanically coupled device was usable up to frequencies of 20 Hz, which was sufficient for the deposition experiments to be described. We also developed an electromagnetically driven needle source, with no mechanical coupling, that operated up to 500 Hz. It can greatly extend the range of measurable rates.

Each reactant, hydrocarbon and oxygen, was delivered by one such oscillating needle source. Both needles were driven by the same oscillator. The hydrocarbon and oxygen needles were synchronized so that when one was aimed at the filament the other was aimed at the bypass. The relative hydrocarbon/oxygen exposure time of the filament could be adjusted by making the oscillator output voltage asymmetric.

The filament was thus exposed to alternate fluxes of hydrocarbon and oxygen whose relative duration could be controlled. Carbon was periodically deposited during exposure to hydrocarbon, and oxidized to CO during exposure to oxygen. The electron emission current rose and fell in response to these reactants and was displayed on an oscilloscope.

The oscillating needle sources injected hydrocarbon or oxygen into a carrier gas whose pressure ranged from .5 to 1 torr. The periodic reactant pressure increments were as low as several tens of microns. We calibrated these increments against the internal needle pressure by a difference measurement using a high volume McCleod gauge. This procedure was faster and simpler than measuring the carrier and hydrocarbon flow rates along with the total pressure.

PROCEDURE

Rates of deposition were determined at low carbon coverage from the oscilloscope trace by measuring the time for the emission current to rise from a low value corresponding to a clean filament to the value corresponding to a coverage of $\sim 1/3$. The coverage could only be found approximately, by assuming a linear relation between coverage and work function in Equ. 1. The measured absolute rates are consequently uncertain, but it is the relative rate behaviour of the sequence of hydrocarbons from methane to octane that is of most interest.

The probability of carbon deposition per molecular impact is of interest as well as the total rate. The rate (in carbon atoms/cm²/sec) can be written as the product of a probability P , a hydrocarbon flux F , and the number N of carbon atoms actually deposited by a decomposing molecule:

$$\text{Rate} = P \times F \times N \quad (2)$$

The rate is measured, and the flux F is calculated from the chopped hydrocarbon pressure, but the number N of contributed carbons is unknown. There is indirect evidence that N may be as small as one. For example, radicals can form on and desorb from hot Pt at a high rate (Fabian and Robertson, 1956). Fragmentation patterns are complex, and a carbon chain may break at any point to give desorption of smaller radicals. This shows that chemisorption of the impinging hydrocarbon is not sufficient to assure trapping of all carbon atoms, and suggests that deposition of even one carbon atom is a rare event. It must be emphasized that N cannot be determined from our experiments, but must be found by independent research. Nonetheless, even though it may not seem to be the natural assumption, we take $N=1$ in order to express rate measurements as deposition probabilities per molecular impact.

EXPERIMENTAL RESULTS

Before presenting the results of our chopped fast flow rate measurements, it is useful to summarize some earlier observations of thermionic emission in a steady fast flow (Halpern, al Mutaz, and Douyon, 1981).

In the nearly free molecule flow regime, ($P \sim 1$ torr for a .0127 cm diameter filament) only a monolayer of carbon deposits when the hot filament is exposed to a steady flow of hydrocarbon. Thereafter the surface is poisoned to further decomposition. An added steady flow of oxygen will oxidize some of the chemisorbed C layer to CO. By adjusting the relative flow of oxygen to hydrocarbon, the carbon coverage, and therefore the emission current, could be maintained in steady state at any value.

A critical ratio of oxygen to hydrocarbon flow was required to drastically reduce the carbon coverage. It could be measured by a "thermionic titration" whose endpoint was signalled by a steep drop in emission current. It was found that the critical oxygen/hydrocarbon ratio increased sharply with hydrocarbon chain length in the series methane to octane.

This finding could indicate that the deposition probability was higher for more complex hydrocarbons. It could also imply that longer chains decomposed to give a configuration of carbon atoms, such as an aromatic ring, that were more difficult to oxidize (Halpern, al Mutaz, and Douyon, 1981). Partly in order to decide between these hypotheses we measured the deposition probability directly.

Accordingly, chopped fast flow rate measurements were carried out for the straight chain alkanes from methane to octane. Rates were measured as a function of hydrocarbon pressure with the sur-

face temperature held constant, and for a fixed hydrocarbon flux at different filament temperatures. Deposition was found to be first order in hydrocarbon flux and the rates decreased with increasing temperature. The deposition probabilities for the series of hydrocarbons at one filament temperature are shown in Fig 2.

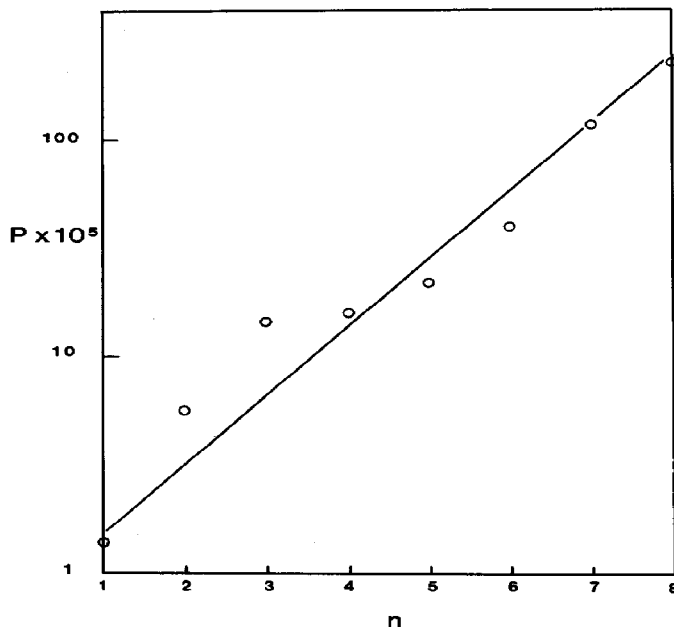


Fig. 2. Plot of carbon deposition probability P versus number n of carbon atoms in molecule. See Equ. 2.

DISCUSSION

We discuss first the strong dependence of deposition probability on alkane chain length. Second, we consider the frequency constraints on the chopped fast flow method.

Deposition probability in chain length

A hydrocarbon molecule does not chemisorb and deposit carbon immediately after striking a hot Pt surface. At low temperature, hydrocarbons adsorb intact on Pt; chemisorption is an activated process (Somorjai, 1977). Desorption of undissociated molecules takes place at 200 - 300 °K while at somewhat higher temperatures, the remaining adsorbed molecules decompose to various bound species. These temperatures indicate both a low physisorption energy and a low activation energy for chemisorption.

On a hot surface the physisorption lifetime can be as short as several picoseconds. Chemisorption will occur only if sufficient internal energy is accumulated during that lifetime. Therefore chemisorption and subsequent carbon deposition depend on the efficient transfer of energy from metal substrate to molecular internal modes in a limited time. However, the characteristic time for energy transfer is larger than the physisorption lifetime. Therefore the deposition probabilities are small as seen in Fig. 2. With this in mind, the sharp dependence of deposition probability on carbon chain length shown in Fig. 2 can be rationalized as follows.

The activation energy must be transferred during a physisorption lifetime τ which is given by

$$\tau = 1/\nu \exp(-E/kT) \quad (3)$$

A range of adsorption energies $2000 < E < 17,000$ cal/mole suffices to describe hydrocarbons from methane to octane. This range may be justified by inference from low temperature thermal desorption spectra of hydrocarbons on Pt or by comparison with the adsorption energies $E(n)$ of n -carbon alkanes on graphite, which are well represented (Young and Crowell, 1962) by the equation

$$E(n) = 850 + 1880 n \text{ cal/mole} \quad (4)$$

for $n = 1$ through 8. Assuming that a similar relation holds for adsorption on Pt, the

physisorption lifetime should be of the form

$$\tau = (1/\nu) \exp(a + bn)/kT \quad (5)$$

Its magnitude lies in the range 10^{-12} to 10^{-11} sec for the alkanes up to octane in the range $1300^\circ\text{K} < T < 1700^\circ\text{K}$, with the values of a and b as in Equ. 4.

Energy is transferred most efficiently to the physisorbed molecule's internal vibrations from electron hole pairs in the metal. The process by which a physisorbed, vibrationally excited molecule loses energy via creation of electron hole pairs is predicted to have a characteristic time of 10^{-11} sec (Persson and Persson, 1980). The characteristic time to excite a molecular vibration of energy hw will be larger by a Boltzmann factor $\exp(hw/kT)$. Therefore desorption is much more likely than energy transfer. However, a large molecule is more likely than a small one to accumulate the activation energy needed for chemisorption during its physisorption lifetime, and then deposit carbon.

The deposition probability P is approximately proportional to the adsorption lifetime of a physisorbed molecule, and will be given by

$$P \propto \exp(a + bn)/kT \quad (6)$$

This explains the steep dependence of P on carbon chain length, as well as the observed decrease in deposition rate with increasing temperature.

The size of the hydrocarbon molecule also affects the chemisorption rate in a way that can be seen via an analogy between a gas phase unimolecular decomposition and the activation of a physisorbed molecule. The hydrocarbon molecule can be regarded as a collection of s coupled oscillators which arrives at and is physisorbed on a hot metal. Excitation of the oscillators occurs by energy exchange with conduction electrons rather than by molecular impacts as in the gas phase. However, in a gas phase unimolecular reaction the energy is delocalized rapidly among the s oscillators (Pilling, 1975). It takes time for energy to accumulate in the right bond, so that reaction does not immediately follow delivery of the correct activation energy. The same delocalization and delay is likely to occur in a physisorbed molecule.

According to the RRK model the unimolecular reaction rate R_{uni} for a molecule composed of s oscillators and bearing energy ϵ greater than the activation energy ϵ_0 is given by (Pilling, 1975)

$$R_{\text{uni}} = (1 - \epsilon_0/\epsilon)^{(s-1)} \quad (7)$$

This rate diminishes, for a given ϵ_0/ϵ , as the molecule becomes larger.

It might then appear that a large molecule need not chemisorb and deposit carbon more readily than a small one despite the longer adsorption lifetime. However, the energy ϵ in Equ. 7 depends on the number of oscillators in the chain. To the extent that the hydrocarbon "lies flat," all identical oscillators can be vibrationally excited by the metal. The energy ϵ must be proportional to s at any time t after adsorption. In a hydrocarbon with n carbon atoms, s is of the order of the number of vibrational degrees of freedom, given by $3x(n + 2n + 2) - 6 = 9n$. For large s , the rate given by Equ. 7 tends to a limit that is independent of n , and even for small carbon chains, the rates are not radically different. The large number of oscillators that can be excited counteracts the effect of energy delocalization. In consequence the dependence of carbon deposition probability on carbon chain length is influenced mainly by adsorption lifetime. We will give a more detailed analysis of these points in a forthcoming paper (Halpern and al Mutaz, in preparation).

Frequency Limitation in Chopped Fast Flow

Reactant chopping is easy to implement in high vacuum, but it might be anticipated that axial diffusion would destroy the "squareness" of the reactant wave in fast flow conditions, and limit the frequency at which modulation is possible. That frequency limit can be estimated by means of the following simple argument.

Suppose that a square wave of reactant is generated at frequency f in a tube through which a carrier gas flows at velocity v . The wave then consists of square reactant pulses of initial width $L = v / 2f$.

During the time of transit t from reactant source to filament, axial diffusion smears the edge of the pulse into a zone whose thickness z is related to the diffusion coefficient D by the random walk equation

$$z = (2Dt)^{1/2} \quad (8)$$

The transit time t will be determined by the flow velocity v and the distance d between the reactant inlet and the filament. The reactant wave will be taken as acceptably square if $z = L/2$. These relations determine an upper frequency limit given by

$$f_{\text{max}} \approx .2(v^3/Dd)^{1/2} \quad (9)$$

At pressures near one torr, typical values in our flow system would be $v \approx 5000$ cm/sec, $D \approx 100$ cm²/sec, and $d \approx 10$ cm. The maximum frequency at which concentration contrast would be preserved against diffusive smudging is then about 2000 Hz, somewhat higher than can be attained with either of our oscillating needle designs. The limit increases with pressure, as expected, though not strongly.

SUMMARY

Chopped fast flow provides a novel extension of molecular beam modulation to flow systems, and permits rate measurements of rapid surface processes in a transient mode without the need for high vacuum. The oscillating needle gas reactant source is one possible method of implementing reactant chopping to high (500Hz) frequencies. The advantages of high product intensity and experimental simplicity should make this approach an appealing one for a variety of surface reaction studies.

In this study we coupled the chopped fast flow technique with thermionic emission as a detector of surface carbon. Measurements of the rate of carbon deposition caused by the decomposition of hydrocarbon molecules on a hot Pt filament show a strong dependence of rate on hydrocarbon chain length. This is consistent with a picture in which the physisorption lifetime on the hot surface limits the time for transfer of activation energy, and leads to a strong influence of molecular size on deposition probability.

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