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GAS PHASE PULSE RADIOLYSIS*   DE88 002981

Charles D. Jonah, Andong Liu and William A Mulac
Chemistry Division, Argonne National Laboratory
Argonne, IL 60439 U.S.A.

INTRODUCTION

Gas phase radiation chemistry is not only a subject but a technique which can be used to study many different phenomena in chemistry and physics. In the last four years there have been more than one hundred papers that have used gas phase pulse radiolysis. These experiments have made use of the ability of radiolysis techniques to create ions, radicals and excited states in concentrations far above what can be determined using other techniques.

Gas phase experiments have been used to understand the fundamental processes of radiation physics and chemistry. To understand the inter-relationships between mobilities, radical densities and localization times, comparisons have been done of the radiolysis of the same systems in liquid and gas. The differences in products and yields that occur when liquid and gaseous hydrocarbons are irradiated have been measured.(Ausloos et al. 1983) The changes in electron mobility between the liquid and the gas phase also give critical information about the physical processes that occur in electron transport.(Jacobsen & Freeman 1986) The thermalization of the electron will determine how far its initial kinetic energy will take it before thermal diffusive processes take over and only gas phase experiments can make such measurements. Thermalization times have been determined for rare gases and simple molecules (Suzuki & Hatano 1986; Warman, et al. 1984). Gas phase studies have shown that the sub-excitation (but not thermalized) electron can react (Denison et al. 1986). This reaction might be similar to the "dry electron" reactions that occur in aqueous systems (Wolff, et al. 1975). Many of the models of how ionizing radiation deposits energy in water use cross sections that are derived from gaseous water (Zaider et al. 1983). Since these models already start with a major unknown, the differences between liquid water and vapor phase water, the experiments which measure the processes that occur in water vapor can potentially provide both insight into the energy deposition process (Quickenden et al. 1986).

Pulse radiolysis has also provided an efficient way of studying physics and chemistry that is not often amenable to other techniques. For example, excited states and excimers of rare gases can be efficiently produced using pulse radiolysis and their spectra, kinetics and formation pathways can be determined. Data prior to 1981 have been reviewed by Sauer (1982) and since that date there has been considerable new work (Mehnert, et al., 1986; Ukai et al. 1986; Tanaka et al. 1985; Shimamori & Fessenden 1981). Electron attachment reactions can be studied easily(Shimamori & Hotta, 1986: Suzuki & Hatano, 1986) including van der Waals molecules (Toriumi & Hatano 1985; Shimamori & Hotta 1986). Ion molecule reactions have been studied, (Cooper et al. 1984). Similar reactions can be important in laser studies (Ueda et al. 1984; Ramirez et al. 1985). Electron transfer reactions in the gas phase can also be measured (Grimsrud et al. 1985).

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Pulse radiolysis has shown itself to be an efficient source of small radicals with which one can do chemistry. These reactions are important in combustion and atmospheric kinetics. Other techniques have different limits on the temperature and pressure range that can be studied. While a large number of radicals have been created (see table 1), only a few such as OH, H and O have been used extensively for kinetic measurements. A large number of experiments have been done over the temperature range of 300K to 450-500K. This range is sufficient to determine the activation energy and simplify the possible reaction mechanisms. Much wider temperatures are useful for understanding certain simple reactions such as OH + CO (Hanrahan 1987; Beno et al. 1985) and for seeing a change in reaction mechanisms (Liu et al., 1987). The choice of possible reaction mechanisms can be further constrained by isotope substitution studies.(Sugawara et al. 1981).

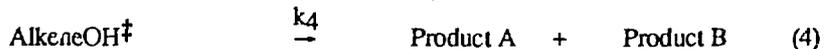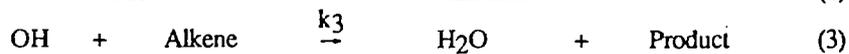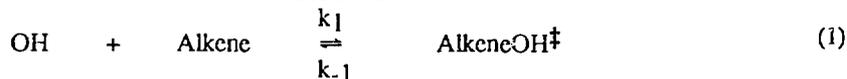| Table	
H and D atoms	
ethylenes, fluoroethylenes acetylenes, ketenes, HI, O_2ClNO	Sugawara et al 1981, Sugawara et al. 1981a, Nielsen et al. 1982, Umemoto, et al. 1984, Lii et al. 1980
O atoms	
Fluroethylenes, ethylene ,propene, 1-butene, butenes, butadiene 2 methyl 2 butene, 2 methyl 2 propene, HO_2	Sugawara et al. 1981a;Umemoto et al. 1980
OH	
cyclohexane, halomethanes, H_2, CO, CO, CH, CO, C_2H_4, 1 3-butadiene, allene, C_2H_4, C_2H_2	Nielsen et al 1986, Nielsen et al. 1984, Hanrahan 1987, Jonah et al. 1984, Beno et al. 1985, Liu et al 1987
HO_2	
Production kinetics, $HO_2(NH_3)$, $HO_2(H_2O)$, HO_2, O	Munk et al. 1986, Lii et al. 1980, 1981, 1979, 1980a
CX_3	
O_2, NO_2	Cooper et al. 1980, Cumming et al. 1980
CH	
alkanes	Bosnali & Perner 1971
CN	
Alkanes	Bullock & Cooper 1972
iC_3H_7 & $iC_3H_7O_2$, C_2H_5 & $C_2H_5O_2$	Munk et al 1986a, Munk et al. 1986b
NH_2,NH	Lesclaux 1984,Fujita 1986

EXPERIMENTAL TECHNIQUES

There have been two major methods for doing gas phase pulse radiolysis experiments - using a Febetron accelerator (Gordon & Mulac 1975; Ramirez et al. 1984; Nielsen et al. 1986; Sugawara et al. 1981) to create high concentrations of radicals very quickly or a linac which will create lower concentrations of radicals (Jonah et al. 1984). The linac however does have an advantage in that the electron beam has more penetrating power so that one can use better insulated ovens and work at higher temperatures. The higher repetition rate makes it possible to do more signal averaging with a linac and thus compensate for the smaller pulse.
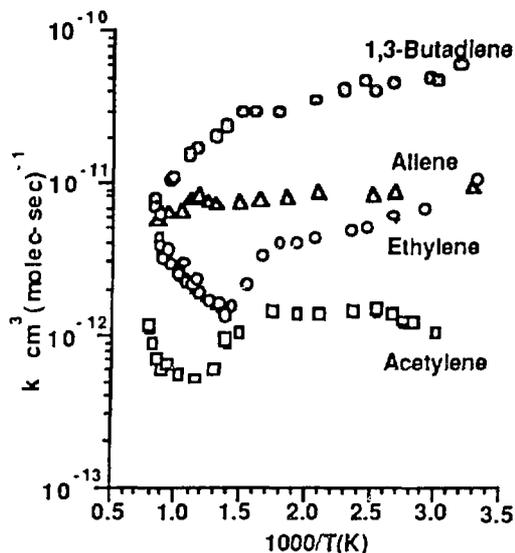
Second order rate constants for the reaction of OH with acetylene, allene, 1,3-butadiene, and ethylene. Measurements made at 1 atm total pressure of argon.

REACTION OF ALKENES WITH OH

There are many interesting chemical systems which could be discussed. The OH + alkene reactions are particularly enlightening because pulse radiolysis uncovered the different reaction mechanisms that occur at different temperatures. The classical Arrhenius behavior is totally absent from these results as one can see from the Figure. There are small negative activation energies, large negative activation energies, and strong positive activation energies. Altogether a result which is not at all like in a physical chemistry book. A mechanism for this reaction is:

$$OH \quad + \quad Alkene \quad \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \quad AlkeneOH^{\ddagger} \qquad (1)$$

$$AlkeneOH^{\ddagger} \quad \overset{k_2}{\rightarrow} \quad AlkeneOH \qquad (2)$$

$$OH \quad + \quad Alkene \quad \overset{k_3}{\rightarrow} \quad H_2O \quad + \quad Product \qquad (3)$$

$$AlkeneOH^{\ddagger} \quad \overset{k_4}{\rightarrow} \quad Product\ A \quad + \quad Product\ B \qquad (4)$$

At room temperature in ethylene, the stabilization of the intermediate in reaction 2 is so efficient that the the reaction all goes to product. As we go up in temperature, the rates decrease because there will be the usual mild negative activation energy which arises due to kinetic effects such as centrifugal barriers. At higher temperatures, reaction 2, the stabilization reaction becomes much less efficient and so k_{-1} becomes much more important. Thus the rate falls off very quickly. At even higher temperatures, reaction 3, the hydrogen abstraction reaction becomes important. This reaction had not been previously measured. This reaction would be expected to have a large activation energy as is seen in this figure.

The rate and activation energy for hydrogen abstraction from ethylene is important in the mechanism for the oxidation of butanes at high temperatures a model for combustion knock.Thus we felt it would be important to verify that the sharp increase in rate for OH plus ethylene is due to the hydrogen abstraction reaction and to determine the rates of hydrogen abstraction reactions in other systems. We made measurements on ethylene and ethylene-d4 (Liu *et al.* 1987a). For this system we found a primary isotope effect as ex-

pected because the H bond is being broken. A simple transition state theory calculation reproduced the experimental results.

To study the rates of hydrogen abstraction from other alkene hydrogens it is necessary that they have no simple aliphatic hydrogens. The energy of aliphatic C-H bonds is considerably lower than the alkene C-H, and the more weakly bound H atom would be extracted preferentially. We thus studied OH with 1,3-butadiene, allene and acetylene.(Liu et al. 1987b) The results are seen in the figure .

For 1,3-butadiene, the addition reaction is faster than the ethylene reaction since there are twice as many places for the OH to add. In addition, the increased number of internal modes of the molecule mean that the alkeneOH[‡] will have a longer lifetime before the OH bond breaks again. Thus reaction 2 will have to become much less efficient before the back reaction becomes important in comparison to the ethylene reaction. This is borne out by the higher temperature at which the sharp decrease in reaction rate occurs. The smaller decrease in the OH addition reaction makes it impossible to directly observe see the hydrogen abstraction reaction; however the upper limit for H atom abstraction rate 3 times faster than in ethylene. The rate constant does start to increase at the highest temperatures measured; the rise is too small for us to determine any details of that reaction.

Allene shows a different type of behavior. The rate constant appears to remain constant as temperature increases. This shows that there must be an additional reaction pathway in which the allene-OH[‡] dissociates but does not form OH and allene again. Molecular beam studies show that there is a zero pressure reaction and indeed that a dissociation product is formed (Slagle et al. 1975).

Acetylene shows even a different behavior. The complex curves are reminiscent of the OH + ethylene results; however the isotope effect is quite different. An inverse isotope effect is seen at intermediate temperatures where acetylene-d2 reacts more quickly than acetylene-h2. This is due to statistical effects which affect the ability of the excited OH-acetylene intermediate to give up energy. At higher temperatures the isotope effect becomes normal - the acetylene-d2 reacts more quickly than the acetylene-h2.

CONCLUSIONS

Gas phase pulse radiolysis can make a significant addition to the study of chemical kinetics and small radical reactions. The ability of the technique to work easily over a large temperature range and at atmospheric pressure has made it possible to bridge the regions where addition reactions dominate to where the addition reaction becomes third order to where the H abstraction reaction becomes important for OH reactions. This temperature range had not been previously studied for any of these systems.

Pulse radiolysis can be particularly effective for studying reactions of HO_2, an important species in atmospheric chemistry, since it can not be easily studied in other techniques. The kinetics are difficult to measure since the absorption coefficient for HO_2 is low. Pulse radiolysis can create sufficiently high concentrations of radicals to observe directly. While there are many reactions of HO_2 which have been studied (Munk et al. 1986), there are many other reactions of HO_2 which can profitably be studied. Particularly valuable would be studies as a function of temperature and pressure. Such studies would complement the low pressure flow tube studies which have been made.

An important parameter of the theory of chemical kinetics is the high pressure rate constant. Pulse radiolysis is well suited for such studies because the yield of products increases strongly at high pressures. Thus this should be a fertile field for study. Already there has been considerable work on H addition to unsaturated alkenes (Kowari et al. 1981). High temperature reactions can be studied efficiently using pulse radiolysis. Such experiments are easier with a linac than with a Febetron because of the higher penetrating

power. It would be interesting for example to see if H abstraction reactions also become important in reactions of H with alkenes and to see at what temperature the addition reaction is no longer in the high pressure limit at 1 atmosphere.

As the table shows there are a large number of possible radicals which have been studied using pulse radiolysis. Many cannot be studied conveniently using other techniques over temperature and pressure ranges which are available to pulse radiolysis. We hope by showing some of the interesting chemical results that have been obtained using pulse radiolysis, that others might become interested in using such techniques to study radical chemistry in the gas phase.

ACKNOWLEDGEMENTS

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