Chem. Educator **2000,** *5,* 317–320

Determination of a Gas-Phase Bimolecular Rate Coefficient Using a Discharge Flow Tube

M. A. Teruel, R. A. Taccone, and S. I. Lane*

INFIQC- Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Pabellón Argentina, Ala 1, 2do. piso. 5000 Córdoba, Argentina, s-lane@fisquim.fcq.unc.edu.ar

Abstract: A laboratory experiment for senior undergraduate students, the determination of the rate coefficient for the reaction of oxygen atoms with hexafluoropropene, is presented. This reaction has the advantage of not having any important secondary reactions. This laboratory experiment introduces the undergraduate physical chemistry student to advanced kinetic techniques and provides a test of the fundamental principles of chemical kinetics.

It is possible to use different experimental techniques to study the kinetics of bimolecular atomic or free-radical reactions with neutral molecules. Flash photolysis, laser photolysis, and flow discharge methods using various detection systems, such as laser induced fluorescence, mass spectrometry, resonance fluorescence, or chemiluminescence, are the major techniques used for the study of the rates of elementary reactions. These reactions are of practical interest, for example, in the modeling of atmospheric chemistry, but they also provide information about the mechanisms of molecular interactions (molecular dynamics).

The fast-flow discharge technique is a valuable tool in gas-phase kinetics because its equipment is relatively inexpensive to build and can be coupled to a number of sensitive detection systems. Furthermore, it is very versatile because it allows changes to be made in experimental variables, such as reactant concentrations and types, and can be used with atoms or radicals.

This technique uses an experimental methodology that can provide undergraduate senior chemistry majors with an opportunity to use experimental equipment such as vacuum systems, mass-flow controllers, and oscilloscopes; to relate topics in physical chemistry, and to interpret and discuss experimental results.

We present the determination of the rate coefficient for the reaction of oxygen atoms with hexafluoropropene. This reaction has the advantage of not having any important secondary reactions. The experimental procedure and approximations used are given in detail in the supporting material*,* along with the necessary equations for the corresponding calculations.

Introduction

Laboratory experiments that illustrate and test the fundamental principles of chemical kinetics are regarded as a mainstay of the physical chemistry laboratory curriculum. Experiments that incorporate the use of current research instrumentation are especially valuable because they give students laboratory experience that anticipates the workplace experience.

The fast-flow discharge technique is a method that can be used to introduce undergraduate physical chemistry students to the advanced experimental techniques used in the study of the reaction kinetics of atoms or free radicals with different molecules [1]. The dynamic techniques have certain advantages over the conventional static ones. These include the ability to change reactants, flows, and atom or radical sources, as well as high sensitivity. These advantages allow the study of a large number of bimolecular reactions (atom–atom, atom–radical, atom–molecule). The occurrence of secondary reactions is reduced by the continuous flow of reactants and the pumping of products out of the tube.

The reaction kinetics of ground state oxygen (^{3}P) atoms with a great variety of reactants has been widely studied for its participation in atmospheric and combustion chemistry. The oxygen atom is certainly a highly reactive species; thus, is not possible to study its reactions in an ordinary static system; a flow method must be employed instead. The triplet (^{3}P) oxygen atoms are easily produced and monitored in the laboratory.

Unsaturated hydrocarbons react in the atmosphere with OH, Cl, Br, O_3, NO_3, and ^{3}P oxygen. The relative importance of these reactions varies, depending on the atmospheric conditions. While triplet oxygen atom reaction rates are often nearly as fast as OH reaction rates, triplet oxygen rarely exceeds 10% of OH concentrations in the atmosphere; hence, its reaction with alkenes rarely exceeds 5% of the OH-loss pathway. Even so, reactions of triplet oxygen are used to accurately model the early stages of smog formation in urban areas when the concentrations of OH and O_3 have not yet built up [2].

The laboratory experiment described here uses a discharge flow apparatus, coupled with chemiluminescence detection to measure the overall rate coefficient for the reaction of triplet oxygen atoms with perhalogenated alkenes. These molecules, at variance with the hydroalkenes, react via a single main pathway, and secondary reactions are negligible. This experiment is used in the physical chemistry laboratory course for senior undergraduate students at Cordoba University, Argentina. The experiment requires about four hours, which includes the analysis and discussion of results. The students are encouraged to read the comprehensive review articles by F. Kaufman [3] and C. J. Howard [4].

S1430-4171(00)06424-3, Published on Web 10/09/2000, 10.1007/s00897000424a, 560317sl.pdf

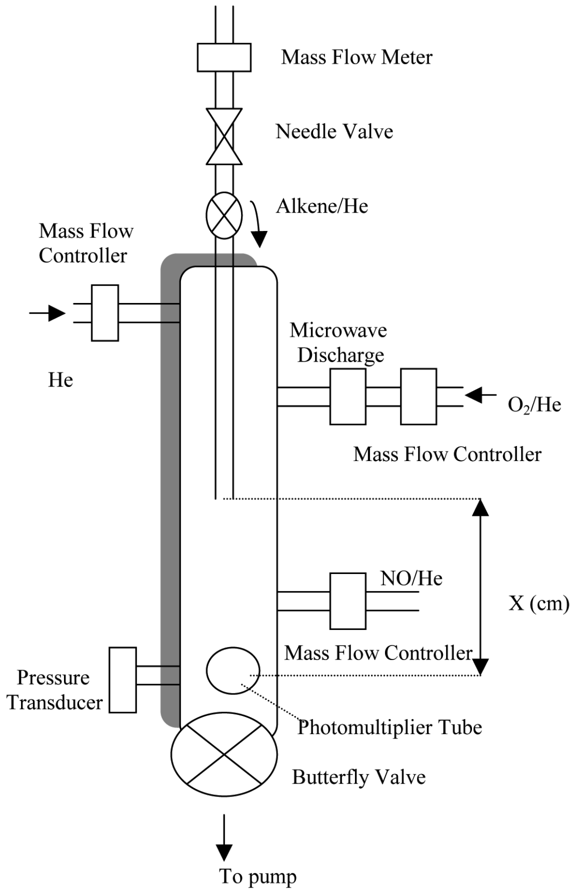

Figure 1. Schematic diagram of the discharge flow reactor used for the study of the reaction of triplet oxygen and alkene at 298 K.

The supporting material outlines the procedure for the measurement and control of flows, the gas-handling system, and the contact time of the reactants and describes the equations used to evaluate the plug-flow approximations, calculate the linear flow velocities, and tobtain the concentrations of the different species (NO, NO_2, O_2, alkene, etc.) involved in the experiment. In addition, the generation and detection of triplet oxygen atoms used in the experiment is described, and the equation to correct the pseudo-first-order rate coefficients by axial and radial diffusion and the error analysis are included.

Experimental Procedure

A schematic representation of the discharge flow apparatus employed in this experiment is shown in Figure 1. The flow system consists of a 1.00-m-long, 2.5-cm internal diameter Pyrex tube, fitted with a sliding Pyrex-glass injector of 0.25-cm internal diameter. Helium is used as carrier gas and is introduced through a side port at the upstream end of the tube. The system is continuously evacuated by a high capacity rotary pump (>60 m^3 h^{-1}). Although not absolutely necessary, a large volume (ca. 10 L) should be placed between the mechanical pump and the flow tube to smooth out flow pulsations caused by cycling of the mechanical pump. A cold trap containing liquid N_2 can be used in order to quench or condense all excited or otherwise corrosive species before they reach the pump. This trap should be of the demountable type for off-system disposal of reagents.

The gas flow to the pump during the experiment is controlled by a butterfly valve, located after the detection zone. The gas-handling system for preparing and delivering the gases to the flow tube consists of three 5- or 10-L Pyrex storage bulbs and a series of glass valves connected to the flow tube manifold. Mass-flow controllers, mass-flow meters, or ball-flow meters coupled to a fine needle valve are used to measure the flow rates of the different reactants. Capacitance manometers are used to measure the pressures in the tube and in the manifold. The oxygen atoms are generated by a microwave discharge on a 1% O_2/He mixture that flows slowly from the storage bulb. The concentration of triplet oxygen atoms is monitored by measuring the visible chemiluminescence produced by their reaction with NO to generate electronically excited NO_2*.

The chemiluminescence signal is detected using a photomultiplier tube (Hamamatsu R636 or 1P28) placed perpendicular to the flow tube. The optimum signal-to-noise ratio is obtained when the photomultiplier tube is polarized at about 1.0 kV. The signal is passed through a wide-band pass filter (λ < 500 nm) before reaching the photomultiplier tube, the output of which is amplified and recorded on an oscilloscope. In order to minimize stray light, it is convenient to cover the flow tube and the detection zone. The inner walls of the tube do not need to be coated for this reaction because heterogeneous loss of ^{3}P oxygen atoms with the wall is negligible in this case.

Results and Discussion

The overall rate coefficients for the reactions of triplet oxygen atoms with perhalogenated alkenes are on the order of 10^{-13} to 10^{-14} cm^3 $molecule^{-1}$ s^{-1}, which make them very suitable for determination by this experimental technique. They have the additional advantage that secondary reactions are not important. To illustrate the procedure we propose the following reaction [5]:

$$O(^3P) + CF_3CF{=}CF_2 \rightarrow \text{products} \qquad (1)$$

1,1,2,3,3,3-hexafluoro-1-propene ($CF_3CF{=}CF_2$) scavenges the oxygen atoms to form products according to the following reactions:

$$O(^3P) + CF_3CF{=}CF_2 \rightarrow CF_2O + CF_3CF \qquad (2)$$

$$O(^3P) + CF_3CF{=}CF_2 \rightarrow CF_2 + CF_3CFO \qquad (3)$$

Reactions 2 and 3 proceed via a short-lived unstable intermediate biradical molecule. It has been reported [5] that the ratio of the rate coefficients, k_2/k_3 is 6.5, indicating that in the oxygen atom addition, the oxygen atom is attached to the less-substituted carbon atom of the double bond of the fluoroalkene [6].

Kinetic Analysis

The experiments are performed under pseudo-first-order conditions so that $[\text{alkene}]_o >> [O(^3P)]_o$. Secondary reactions that might significantly decrease the concentration of oxygen atoms are negligible (see the supporting material). A known excess of NO is introduced to monitor the concentration of the oxygen atoms according to the following air-afterglow reaction:

$$O(^3P) + NO + M \rightarrow NO_2^* + M \qquad (4)$$

$$NO_2^* + M \rightarrow NO_2 + M \qquad (5)$$

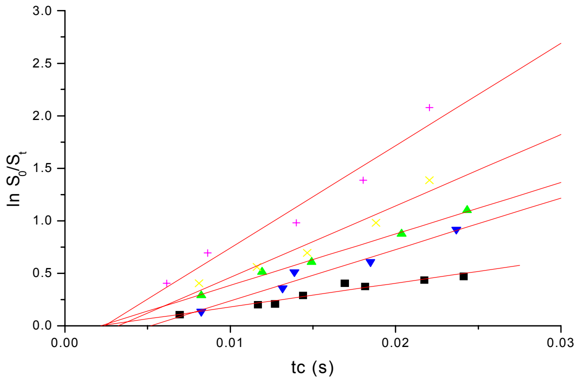

Figure 2: Pseudo-first-order plots for the reaction $O(^3P)$ + $CF_3CF{=}CF_2$ at different alkene concentrations.(■ $[CF_3CF{=}CF_2] = 3.06 \times 10^{14}$ molecule cm^{-3}; ▼$[CF_3CF{=}CF_2] = 6.13 \times 10^{14}$ molecule cm^{-3}; ▲ $[CF_3CF{=}CF_2] = 9.17 \times 10^{14}$ molecule cm^{-3}; × $[CF_3CF{=}CF_2] = 15.32 \times 10^{14}$ molecule cm^{-3}; +$[CF_3CF{=}CF_2] = 19.70 \times 10^{14}$ molecule cm^{-3}.

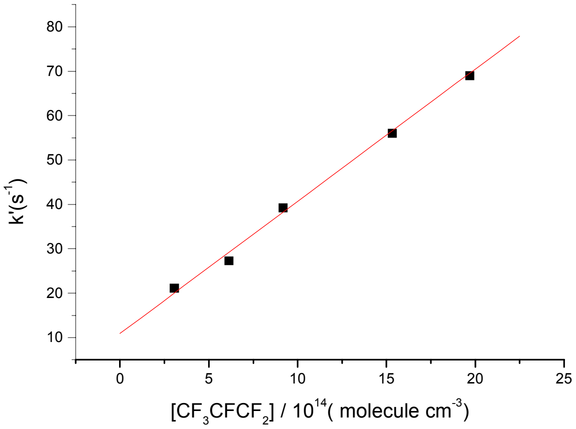

Figure 3: Second-order plot for the reaction $O(^3P) + CF_3CF{=}CF_2$.

where M represents any molecule acting as a third body to favor recombination or to remove the excess energy.

The concentrations of NO used are such that a chemiluminescence signal is observed without significantly affecting the concentration of oxygen atoms. The NO_2 molecules formed rapidly regenerate NO according to

$$O(^3P) + NO_2 \rightarrow NO + O_2 \qquad (6)$$

so that the NO concentration remains almost constant ($k_6 = 9.7 \pm 1.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K) [7].

Kaufman [8] demonstrated that the intensity of the chemiluminescence signal, S_o, of the air-afterglow reaction is proportional to the product of NO and triplet oxygen concentrations and independent of the total pressure, so that $S_o \propto [NO][O(^3P)]$. Because [NO] is constant, the intensity of the chemiluminescence signal at selected points down the tube is a relative measure of the concentration of triplet oxygen.

The depletion of ^3P oxygen atoms due to reaction with NO from the point of its inlet to the tube up to the detector is calculated to be lower than 4%. The contributions to the loss of oxygen atoms through secondary reactions are, in general, lower than 0.01% for reaction 7 and lower than about 3% for reaction 8 using a reasonable wall recombination rate on glass ($k_w \approx 1$ to 5 s^{-1}).

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (7)$$

$$O(^3P) + \text{wall} \rightarrow \text{Products} \qquad (8)$$

For this reason, the variation of the concentration of oxygen atoms with time can be written as

$$[O(^3P)]_t = [O(^3P)]_o\, e^{-(k\,[\text{alkene}]_o + k_d)t} = [O(^3P)]_o\, e^{-k't}$$

where $[O(^3P)]_o$ represents the concentration of oxygen atoms in the absence of the alkene; $[O(^3P)]_t$ is the concentration of oxygen atoms after reaction with the alkene over time t; k_d is the first-order rate coefficient for $O(^3P)$ disappearance by diffusion out of the reaction area, reactions with background impurities, or wall losses; k is the second-order rate coefficient; and k' is the pseudo-first-order rate coefficient.

The above equation can be expressed as:

$$\ln\frac{[O(^3P)]_o}{[O(^3P)]_t} = k't = \ln\frac{S_o}{S_t}$$

So that:

$$\ln\frac{S_o}{S_t} = k't$$

where S_o is the chemiluminescence signal without reactant and S_t is the chemiluminescence signal after addition of reactant at a fixed time of contact (t_c). According to this equation, a plot of $\ln(S_o/S_t)$ against t_c should be linear with slope equal to $k[\text{alkene}]_o + k_d$ with zero intercept. Note, however, that the results shown in Figure 2 present an ordinate, a behavior usually observed in this kind of experiment that probably arises from simplifications involved in the kinetic treatment. The pseudo-first-order rate coefficient, k' can be further corrected for axial diffusion and plug-flow deviations (see supporting material).

Second-Order Overall Rate Coefficient

The second-order overall rate coefficient for the proposed reaction is obtained from experimental measurements of the intensity of the chemiluminescence signal. Thus, the pseudo-first-order rate coefficient, k', for a given concentration of alkene is obtained from the slope of the straight line of a plot of $\ln(S_o/S_t)$ as a function of the contact time, t_c, (Figure 2). A least-squares fit of the experimental values of a plot of k' versus [alkene] (Figure 3) yields (from the slope of the line) the second-order overall rate coefficient, k, for reaction 1. The systematic errors in the measurement of temperature, gas flows, etc. are, in general, lower than 2σ [3, 4] (see supporting material).

The value of the second-order intercept provides an estimation of k_d. An intercept value lower than 20 s^{-1} is desirable [3]. It is important to evaluate the contribution to the error of the different variables that are used in the rate coefficient calculation.

Concluding Remarks

The experiment described is fast, simple and yields reliable results. It can be conveniently performed by teams of 5 or 6 students. It introduces students to laboratory applications of chemical kinetics and spectroscopy, which are covered in all physical chemistry courses. The students learn to handle gases in a vacuum line, some basic concepts of fluid dynamics (measurement and control of flows, determination of linear flow velocities and calculation of concentrations of different species in dynamic systems), and how to generate and detect atoms or radicals. They gain experience with fluorescence and chemiluminescence detection and learn to operate detection equipment (oscilloscope, photomultiplier tubes, high-voltage sources, microwave generators, and pressure and flow meters).

This experiment can motivate the discussion of more advanced topics in physical chemistry and stimulate student interest in the calculation of overall rate coefficients for bimolecular reactions from experimental results and the analysis of the influence of the different assumptions and approximations performed in the calculations (i.e., the estimate of the corresponding error). Finally, it allows discussion of the influence of different substituents on the reactivity of organic molecules towards atoms or radicals that are produced in the flow discharge tube (for example, triplet oxygen, OH, doublet chlorine) and the interpretation of the probable reaction mechanism.

Acknowledgment. The financial support of CONICET (Argentina), CONICOR and SECyT-UNC (Córdoba, Argentina), and the British Council is gratefully acknowledged. M.A.Teruel thanks CONICET for a fellowship.

Supporting Materials. One supporting file is available. A laboratory handout out for students (http://dx.doi.org/10.1007/s00897000424b).

References and Notes

1. (a) Provencher, G. M. *J. Chem. Educ.* **1981,** *58,* 1024–1028; (b) Marcotte, R. E. *J. Chem. Educ.* **1980,** *57,* 388–389.; (c) Pilling M. J.; Seakins P. W. *Reaction Kinetics;* Oxford University Press: New York, 1995.
2. Killus, P.; Whitten, G. Z. *Environ. Sci. Technol.* **1984,** *18,* 142–148.
3. Kaufman, F. *J. Phys. Chem.* **1984,** *88,* 4907–4917.
4. Howard, C. *J. Phys. Chem.* **1979,** *83,* 3–9.
5. (a) Saunders, D.; Heicklen, J. *J. Phys. Chem.* **1966,** *70,* 1950–1958. (b) Saunders, D.; Heicklen, J. *J. Am. Chem. Soc.* **1965,** *87,* 4062–4068.
6. Cvetanovic, R. J. *Advances in Photochem.* **1963,** *1,* 115–182.
7. DeMore, W. B.; Sander, S. P.; Howard, C. J.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Hampson, R. F.; Kurylo, M. J.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling;* J.P.L. Publication, NASA, **1997,** 97-4.
8. Kaufman, F. *Prog. React. Kinet.* **1961,** *1,* 1–39.