equilibrium constant is essentially an enthalpy effect, with *cis* being the thermodynamically more stable, in agreement with Craig and Entmann's findings. The heat of hydrogenation for $C_2H_2F_2$ is not known, but could be established from the experimental activation energies and Lin and Laidler's correlation[6] that $E_a \sim 2(-\Delta H°\text{hyd})$.

A recent study of propylene-1-d_1 isomerization[14] gave $k(cis\rightarrow trans) = 10^{13.16}e^{-61,300/RT}$ sec^{-1}. An A factor of 10^{13} has been estimated[15] for $C_2H_2D_2$ isomerization. Hence the value of $10^{13.17}$ for *cis*→*trans* isomerization of $C_2H_2F_2$ is quite reasonable.

An interesting kinetic system for comparison is N_2F_2, for which a shock tube isomerization study[16] led to a *cis–trans* rate constant of $10^{14}\exp(-32{,}000/RT)$ sec^{-1}. Although this value was based on just five data points and the activation energy value is not well established, isomerization involving a linear transition state is possible for N_2F_2; and this might well allow a lower energy process than is possible with the twisted transition state which operates in carbon double bond systems.

Schlag and Kaiser[17] have measured *trans–cis* isomerization rates in perfluorobutene-2 and found a unimolecular constant of $k = 10^{13.53}e^{-56,400/RT}$ sec^{-1} over a range of 705–750°K. They explain the lower activation energy, relative to 2-butene, as due to destabilization of the π system caused by inductive effects of the adjacent F atoms. It is surprising, then, that difluoroethylene has essentially the same activation energy for isomerization as has 2-butene. Examination of perfluoro-2-butene by the shock tube relative rate method thus appears justified, since results in the same temperature range which are obtained by use of the same experimental techniques should be readily comparable.

Flowers and Jonathan[14] have called attention to the small amount of reliable data on geometrical isomerization, and the authors of the references cited above discuss the difficulty of separating the homogeneous isomerization reaction from significant contributing heterogeneous or bimolecular processes. The shock tube technique has been shown in this study to allow rather direct and uncomplicated access to the unimolecular high-pressure regime. Relative rate measurements eliminate much of the usual scatter in the experimental data (mostly the scatter is due to imprecise reflected shock temperature) and also simplify requirements for, and thus construction of, the shock tube. The instrument described in this paper was built entirely by the authors, using only a scantily equipped machine shop, at a total cost of under $1500, excluding oscilloscope and chromatograph. This sort of instrument and study could easily be adapted to advanced undergraduate laboratory work.

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Catalytic Recombination of Oxygen Atoms on Metal Surfaces in the 10^{-4}–10^{-6} Torr Pressure Range

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Abstract: Reaction kinetic studies were made at 10^{-4}–10^{-6} Torr total pressure on the recombination of oxygen atoms on metal surfaces. A flow system using an auxilliary reaction system at 0.1–1 Torr was used as an oxygen atom source with 10–20% oxygen mixed with argon. The ratio of O/O_2 varied from 2 to 1/2. Initially, ozone production over a long period of time was assumed equivalent to the O atoms surviving the reaction chamber. Chemiluminescence was observed and used as a measure of oxygen atoms. A technique was developed for rapid determination of recombination efficiencies (γ) for O atoms on various metal surfaces. Results for a variety of test specimens are presented. The sensitivity for O-atom detection for these methods is limited to a partial pressure of O atoms of 10^{-8} Torr.

Numerous investigators have performed experiments to detect and measure the heterogenous atom recombination on surfaces. Although the experimental procedures employed varied widely in detail, they may be classified according to the method by which the gaseous atom density was estimated. Direct measurements of atom density have been made using the Wrede–Harteck gauge,[1–4] the reduction of molybdenum trioxide by gaseous hydrogen atoms,[5] and more recently paramagnetic resonance.[6–9] Indirect methods of es-

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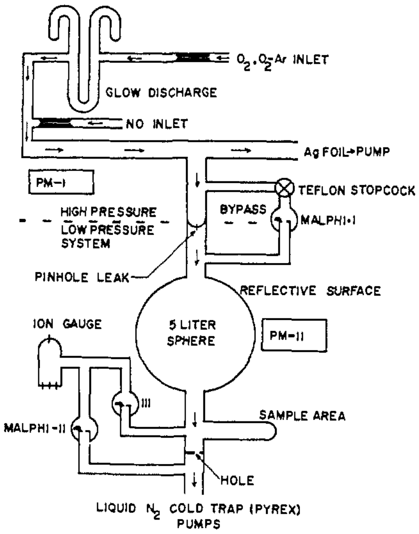

Figure 1. A schematic of the apparatus. PM-I (photomultiplier I) is used to monitor O-atom concentration and trigger observation of PM-II. The MALPHI (Magnetically Actuated Low Pressure Hand Indexed) valves were specifically designed to avoid exposing the system to anything but glass. The bypass of the pinhole leak permits conditioning of the low-pressure system to O atoms in the 10^{-2} Torr pressure range.

timation involved the use of probe thermocouples or heat input wires[10-16] to measure the temperature rise resulting from the atom recombination on the surface of the probe or wire. Most investigations to date have been performed in the pressure range of 0.1–1 Torr using either gaseous hydrogen or oxygen recombining on various metal, nonmetal, oxide, and halide[12] surfaces.

The present effort is the extension of the data to the 10^{-4} Torr and lower pressure region. At these low pressures the kinetics involved are not apparent. In the previous cited work, first-order reaction rates are generally applicable. This implies that the rate of recombination is proportional to the concentration of the species in the gas phase which collides with the surface. Thus, the rate of recombination must be proportional to the area of the exposed surface. The data obtained to date are not sufficiently precise to verify these assumptions, but it is useful as a means of comparing experimental results (Table I) as cited in the literature.[16] The results, given as recombination coefficients or efficiencies (γ), imply an average number of collisions with the surface before recombination occurs.

The gases in the pressure region within which these studies are made have free paths much greater than the laboratory apparatus. Since atomic oxygen colliding with any material may be destroyed, it is not unusual to observe a total loss of any reactive species when special care is not taken. The approach used here was to extrapolate from an experimental arrangement used successfully several years earlier in the 10^{-2} Torr pressure range.[17,18]

Table I. Typical Recombination Efficiencies for Oxygen Atoms on Various Surfaces at Room Temperature

Surface	γ
Metals	
Gold plate	0.0060
Gold sheet	0.0033
Al (commercial untreated foil)	0.0032
Al 1100 (rough surface)	0.050
Ta	0.0058
Stainless steel[a]	0.036
Ni	0.040
Ag[b]	>0.05
Ti (clean surface)[c]	>0.05
Ti (oxidized surface)[c]	<0.001
Nonmetals	
Glass (Pyrex)	<0.0001
Enamel chips	0.016

[a] Early results from the 7.5-m stainless steel sphere at Bonn indicated a recombination efficiency of 0.01.[21] [b] The silver surface becomes oxidized and more reactive with time. [c] $Ti + O \rightarrow TiO\uparrow$ (evaporates); $TiO + O \rightarrow Ti + O_2$; and $TiO + O \rightarrow TiO_2$. TiO_2 is apparently inert, but TiO volatilizes and can cause O-atom consumption for an extended period.

Experimental Section

An oxygen atom stream was generated by a glow discharge in the 1 Torr pressure region and the O-atom concentration determined and monitored by titration with NO_2 and NO in this[19] higher pressure manifold. A small sidestream is directed into the very low-pressure reaction system operating in the 10^{-5} Torr or less region. The apparatus is shown schematically in Figure 1. Oxygen atoms were initially shown to survive the flow system when no sample was present by freezing the radicals with liquid helium. The ozone produced quantitatively on warming was then measured. Silica gel or a Linde 5A absorbent at liquid nitrogen temperature was also used to freeze out the ozone with basically the same results. This observed formation of ozone confirmed without question the existence of the O-atom stream.

The O-atom concentration in the low-pressure chamber was monitored by measuring the light intensity produced by the chemiluminescent reaction of nitric oxide with O atoms ($NO + O \rightarrow NO_2 + h\nu$), using an EMI 9502SA photomultiplier maintained at the temperature of a Dry Ice–isopropyl alcohol slurry. The output of the photomultiplier was amplified using a Keithley 610BR electrometer with the output displayed and photographed on an oscilloscope. In Figure 1 details are not shown of the light traps (Wood's horns). A specially designed all-glass (MALPHI) valve was used extensively to avoid interaction with O atoms.

Data were taken for a specific metal by switching off the discharge which stopped abruptly the O-atom input to the low-pressure reaction system. The decay of the light emission with time was displayed on the oscilloscope and the rate was indicative of the recombination efficiency.

Gases used were obtained from the Matheson Corp. The oxygen–argon mixtures were supplied premixed. The gases were of sufficient purity except for the nitric oxide which was purified by distillation from liquid oxygen to liquid nitrogen.

Summary of Experimental Results

Gold, silver, stainless steel, and titanium all interact significantly with oxygen atoms. Insulating materials such as enamel chips were found to interact with the O atoms as strongly as the metals tested. The most inert

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material to date is glass (Pyrex) of which the apparatus is constructed. Typical recombination efficiencies for oxygen atoms on various surfaces at room temperature are given in Table I.

In each case the decay of the afterglow was observed to decrease exponentially with time indicating that the oxygen atoms were destroyed by a first-order process proportional to the O-atom concentration. This was true when NO was added as a stable reactant and the light intensity of the reaction ($NO + O \rightarrow NO_2 + h\nu$) monitored. This was also true when SO was used to generate the light by the reaction $SO + O \rightarrow SO_2 + h\nu$ where the oxygen atoms must generate the SO *via* the reaction $COS + O \rightarrow CO + SO$.[18] With no sample present the light intensity showed a second-order loss as might be expected since the O atoms and SO were pumped away simultaneously. This result was quite rewarding because it indicated that extrapolation to even these very low pressures was reasonable for the kinetic mechanism postulated for the chemiluminescence.

Discussion

The fraction of oxygen atoms lost on collision with a metal surface (γ) was determined from the decay curve of light intensity as a function of time. The apparatus was operated as a steady-state flow system with the decay occurring when the oxygen atom supply to the reaction vessel was interrupted by turning off the discharge. If the system were clean and no metal specimen present, the oxygen atoms would effuse out of the reaction vessel through the hole (Figure 1) rather than suffer any significant loss due to recombination in the vessel. Since the mean free path of the atoms was much greater than the dimensions of the vessel, the effusion rate corresponded to the simple kinetic formula

$$N/n = cA/4 \tag{1}$$

where N = number atoms per second passing through the hole of area A, n = atom density per cm^3 in the vessel, c = average velocity of the atoms in cm/sec, and A = area of the hole in cm^2.

The decrease in the number of oxygen atoms, $-\mathrm{d(O)}/\mathrm{d}t$, from the total number, (O), was $n_O cA/4$. Since $(O) = n_O V$, where V was the volume of the vessel, the above relation may be given as

$$\frac{-\mathrm{d(O)}/\mathrm{d}t}{\mathrm{(O)}} = \frac{n_O cA/4}{n_O V} = \frac{cA/4}{V} \tag{2}$$

Rearranged and integrated eq 2 becomes

$$\ln \mathrm{(O)}_1/\mathrm{(O)}_2 = (cA/4V)(t_2 - t_1) \tag{3}$$

The decay half-life was obtained *via*

$$\ln 2 = (cA/4V)t_{1/2}{}^0 \tag{4}$$

Varying the hole size (A) changed the effusion rate of oxygen atoms proportional to the intensity of chemiluminescence observed. Since this decay was exponential, its half-life ($t_{1/2}{}^0$) was readily measured. In Table II are shown the decay times ($t_{1/2}{}^0$) and steady-state pressures for a given throughput of gas and fixed volume with no sample present. Table II is derived by simple calculation from the kinetics, but was verified by laboratory experiments. A more rapid decay was observed with samples present, and this increase in decay rate was a measure of γ.

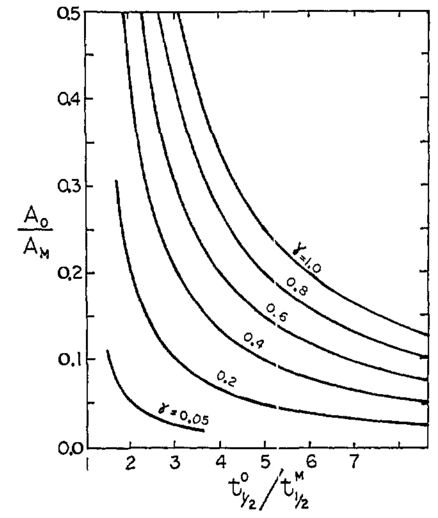

Figure 2. An illustrative plot of A_0/A_m *vs.* $t_{1/2}{}^0/t_{1/2}{}^m$ for various values of γ.

The relatively different effusion rates of O atoms and argon due to their different masses and hence velocities (c) in eq 1 do not effect the measured half-lives.

Table II. Decay Half-Lives of Light Intensity and Steady-State Pressure for a 6-l. Flask with a Throughput of 4 × 10^{14} Particles/Sec

Area, cm^2	$t_{1/2}$, sec	Pressure,[a] ×10^6 Torr
1.0	0.38	1.0
0.38	1.0	2.6
0.25	1.52	4.0
0.2	1.9	5.0
0.1	3.8	10.0

[a] The pressure readings on the ion gauge will not be entirely correct since the oxygen oxidizes parts of the gauge resulting in inaccuracies.

The vessel used experimentally had a volume of 6 l. with the area of the hole variable. The half-life of the O atoms in the vessel (the half-life of light intensity) was

$$t_{1/2}{}^0 = \frac{V \ln 2}{(cA/4)} = \frac{(6 \times 10^3)}{(1.6 \times 10^4)A} = \frac{0.38}{A} \text{ sec} \tag{5}$$

since the pumping speed corresponded to O atoms effusing out of the flask through a 1-cm^2 hole was (6.3 × 10^4) (1)/4 or 1.6 × 10^4 cm^3/sec.

For a metal surface of area, A_m, introduced into the system and destroying O atoms with an efficiency γ, the above analysis was modified such that if eq 4 was set equal to eq 5 one obtained

$$\left(\frac{cA_0}{4V}\right)t_{1/2}{}^0 = \left(\frac{cA_0}{4V} + \frac{cA_m\gamma}{4V}\right)t_{1/2}{}^m \tag{6}$$

or

$$t_{1/2}{}^0 = (1 + \gamma A_m/A_0)t_{1/2}{}^m$$

which is equivalent to

$$\frac{A_0}{A_m} = \frac{\gamma}{(t_{1/2}{}^0/t_{1/2}{}^m) + 1} \tag{7}$$

Thus if one measures a decay half-life without a metal sample present ($t_{1/2}{}^0$) which corresponds to an effective hole area (A_0) as well as a $t_{1/2}{}^m$ for a known A_m, one may use eq 7 to find a precise γ or Figure 2. Equation 7 is plotted in Figure 2.

In an earlier work[17] it was recognized that back-diffusion was a major problem. It was easily avoided by use of a long path length (approximately 3 m) between the reaction vessel and the pumping system itself. Unfortunately back-diffusion was considered to be an obvious gas kinetics problem, and it was not specifically pointed out in the published article. This and similar problems have arisen in low-pressure studies of this type and have frequently been overlooked. In the experiment reported here back-diffusion is avoided by use of an effusion orifice where a high pressure ratio is maintained across the hole (Figure 1).

In several studies the recombination of oxygen atoms on a surface or back-diffusion itself has reduced the steady-state O-atom concentration at a given point in the system. Titration results for example are then in error since the reaction used ($NO_2 + O \rightarrow NO + O_2$) is very fast and results in titrating all the oxygen atoms flowing into a reaction chamber. The number in the steady state, however, is normally reduced by consumption on the walls of the vessel and by back-diffusion of recombined oxygen.

The results presented here are compatible with the simple two-body reaction mechanism propounded in earlier papers.[17,20] This does not eliminate the possibility of two operating reaction mechanisms, the second being the three-body reaction with an intermediate excited state. Other low-pressure experiments reported in the literature which support the latter mechanism frequently fail to account for such problems as back-diffusion. The work at Bonn[21] does support our earlier conclusions.

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Molecular Modulation Kinetic Spectrometry. ClOO and ClO_2 Radicals in the Photolysis of Chlorine in Oxygen

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Abstract: By means of the new molecular modulation method, the gas-phase absorption spectra of the peroxyl radical ClOO has been observed between 2300 and 2600 Å (ultraviolet) and between 1430 and 1460 cm^{-1} (infrared). This radical was produced by the photolysis of Cl_2 in the presence of O_2. The ultraviolet spectrum of the ClO radical was also observed, but its infrared spectrum could not be obtained by this method. By direct observation of these two intermediates, a detailed kinetic study was carried out, in which radical half-lives were inferred from observed phase shifts between the square-wave photolyzing light and the radical concentration. To enhance the weak signals from the low concentration radicals, the data were put in digital form and long-term averaging was carried out. The mechanism built up by previous workers was modified slightly to give a ten-step mechanism, which is in excellent agreement with observations. By combining other rate measurements, thermodynamic data, and the present results, seven out of the ten elementary rate constants were evaluated, and a product-and-ratio of the other three was evaluated as one term. The absolute cross section for absorption of infrared and ultraviolet radiation by ClOO was determined.

Porter and coworkers[1-3] postulated the ClOO peroxy radical as a short-lived precursor to the ClO radical which they detected in the flash photolysis of chlorine–oxygen mixtures. On the basis of the very small temperature coefficient of ClO formation, Porter and Wright[2,3] concluded that the only plausible reaction by which ClO could be formed is

$$Cl_2 + h\nu \xrightarrow{a} 2Cl$$

$$Cl + M + O_2 \underset{c}{\overset{b}{\rightleftarrows}} ClOO + M \qquad (1)$$

$$ClOO + Cl \xrightarrow{d} 2ClO$$

They observed that the decomposition of ClO to Cl_2 and O_2 occurs relatively slowly, has a negligible activation energy, and is second-order with respect to ClO, and the rate is independent of Cl_2, O_2, and total gas pressures

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