

ultraviolet spectrum of ClO have been studied repeatedly. Other investigations have agreed that ClO reverts to Cl₂ and O₂ by a process second order in ClO, but the reported second-order constants have shown large variations between authors. We have confirmed and characterized the foreign gas catalysis of this process, which accounts for much of this discrepancy.

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Administration, Department of Health, Education, and Welfare, Public Health Service, Grant AP-00104. The original intention was to use the well-known chlorine-oxygen system and the well-characterized ClO intermediate as a calibration for the new molecular modulation method. With the discovery of ClOO and new kinetic features, the intended brief calibration was expanded to this full study. We are deeply grateful to both the AEC and the National Air Pollution Control Administration for long-term support of this work, and to the National Science Foundation for a Traineeship for E. D. M.

Isotope Exchange Rates. VII. The Homogeneous Atom Switching Reaction between Oxygen Molecules

H. F. Carroll and S. H. Bauer

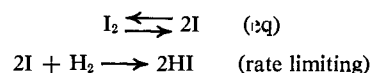
Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received June 26, 1969

Abstract: The atom switching process, $^{32}\text{O}_2 + ^{36}\text{O}_2 = 2^{34}\text{O}_2$, with the reactants highly diluted in argon, was studied behind reflected shocks in single-pulse shock tubes over the temperature range 1150–1600°K. Oxygen mole fractions varied from 0.0005 to 0.02, and the total density ranged from 1×10^{-2} to 4.5×10^{-2} mole l.⁻¹. The $^{36}\text{O}_2$ gas was prepared by electrolyzing 97.6 atom % ^{18}O water. Compositions of the reactant and product mixtures were estimated with a CEC No. 21-103 mass spectrometer. The exchange rate data were fitted equally well by two empirical rate expressions: $d[^{16}\text{O}^{18}\text{O}]/dt = 4 \times 10^{12} \exp[-(41 \pm 4)/RT][^{32}\text{O}_2][^{36}\text{O}_2]$ moles l.⁻¹ sec⁻¹, and $d[^{16}\text{O}^{18}\text{O}]/dt = 7 \times 10^{10} \exp[-(39 \pm 4)/RT]([^{32}\text{O}_2] + [^{36}\text{O}_2])^2$ moles l.⁻¹ sec⁻¹. The possible effects of impurities (particularly of N₂ and D₂) were tested and shown to be of no consequence. Experimental conditions exclude the possibility that the measured exchange was due to an atomic abstraction mechanism. These rate expressions can be rationalized on the basis of a two-level vibrational excitation model, when slightly different assumptions are introduced. The assumptions are consonant with energy-transfer efficiencies reported for oxygen-oxygen collisions but not with the reported vibrational relaxation times for oxygen-argon collisions. The possible reasons for this disagreement are discussed, and the differences between the oxygen exchange and other homogeneous exchanges are also examined.

Four-center metatheses are used infrequently as elementary steps in kinetic mechanisms, yet they constitute a reaction type which conceptually cannot be ignored. In conventional kinetic investigations, wherein radicals play a dominant role (generated not infrequently by unspecified initiating steps, such as stray irradiation or surface reactions), molecules switch atoms by displacement or by abstractions which have comparatively low activation energies. However, because the four-center homogeneous metathesis is possibly the oldest elementary step postulated by chemical kineticists, it is challenging to discover conditions wherein it dominates the course of a reaction, and to determine the energetic and geometric parameters which control the relative efficiencies for such reactions in molecular encounters.

After half a century, during which many generations of chemists were told that the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ was an experimentally demonstrated example of a four-center homogeneous metathesis (perhaps the only one), Sullivan¹ showed that (a) above $\approx 800^\circ\text{K}$ most of the HI was produced *via* a chain, analogous to the

course followed by the other hydrogen-halogen reactions; and (b) at lower temperatures, both the thermal and photochemical data are best interpreted in terms of a two-step process



However, almost concurrently the potential of shock tubes for the study of strictly homogeneous high-temperature reactions was recognized^{2,3} and exploited for the investigation of several H/D atom exchanges under conditions which indicated, with a high degree of probability, that the products pass through a four-center transition state.⁴⁻⁹ In two more investigations, using

(1) J. H. Sullivan, *J. Chem. Phys.*, **46**, 73 (1967), and previous publications.

(2) H. S. Glick, J. J. Klein, and W. Squire, *ibid.*, **27**, 850 (1957).
 (3) S. H. Bauer, *Science*, **141**, 867 (1963).
 (4) S. H. Bauer and E. L. Resler, Jr., *ibid.*, **146**, 1045 (1964).
 (5) (a) A. Lifshitz, C. Lifshitz, and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 143 (1965); (b) A. Burcat and A. Lifshitz, private communication.
 (6) (a) S. H. Bauer and E. Ossa, *J. Chem. Phys.*, **45**, 434 (1966); (b) A. Lifshitz and A. Burcat, *ibid.*, **47**, 3079 (1967); (c) D. Lewis, Cornell University, unpublished results.
 (7) W. S. Watt, P. Borrell, D. Lewis, and S. H. Bauer, *J. Chem. Phys.*, **45**, 444 (1965).
 (8) A. Burcat, A. Lifshitz, D. Lewis, and S. H. Bauer, *ibid.*, **49**, 1449 (1968).
 (9) D. Lewis and S. H. Bauer, *J. Am. Chem. Soc.*, **90**, 5390 (1968).

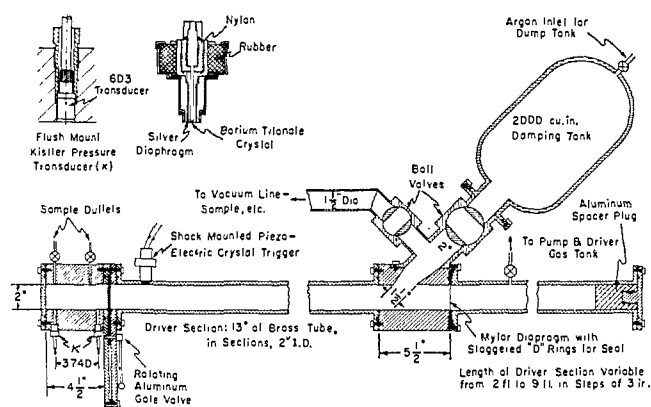


Figure 1. Schematic drawing of the 2-in. shock tube.

the same technique, the switching of heavy atoms [$N_2 + N_2$;¹⁰ $CO + CO$]¹¹ was investigated. In all cases the argon diluent clearly played a significant role, such that while the total order for the reaction was 2, the partial order with respect to argon was 0.5–1.0. Both qualitatively and quantitatively these observations are consistent with a "vibrational excitation" model, *i.e.*, that the probability for atom exchange during collision is substantial only when one of the molecules is vibrationally excited to some minimum or higher level; then the rate-limiting process proves to be the rate of repopulating the critical vibrational levels. For many decades, in the absence of properly designed experiments, it had been assumed as an unwarranted extension of the principle of equipartition that in all elementary bimolecular steps all the molecular energy modes contribute with comparable efficiency toward energizing the transition state. This is in contrast to the accepted model for unimolecular reactions which requires that the activation energy accumulate in certain coordinates before there is a significant probability that the corresponding geometric adjustments occur.

The shock tube investigations already reported, while providing the impetus for a reexamination of the bimolecular collision model, are incomplete in several respects. In the seven cases studied all the reactants were in singlet electronic states, with a wide energy gap between the ground and the first excited electronic states. This report concerns the homogeneous exchange $^{32}O_2 + ^{36}O_2 \rightarrow 2^{34}O_2$, studied by essentially the same technique that was used for the other metatheses. It is anticipated that whatever differences appear relative to the exchange reaction will also appear relative to vibrational energy-transfer processes.

To complete the historical introduction attention is called to the many oxygen atom exchange reactions which have been investigated in heterogeneous systems, wherein the kinetics are intimately bound up with the type of surface used, its detailed composition, and structure. Winter and coworkers,¹² in a series of papers on exchange reactions over a variety of oxide surfaces, found that the activation energy for the exchange process varied from 19 to 38 kcal/mole, depending on the catalyst. They also observed that for some oxides above 400°, the activation energy decreased abruptly to

(10) A. Bar-Nun and A. Lifshitz, *J. Chem. Phys.*, **47**, 2878 (1967).

(11) A. Bar-Nun and A. Lifshitz, *ibid.*, in press.

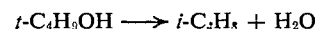
(12) E. R. S. Winter, *J. Chem. Soc.*, 3824 (1955), and previous publications.

less than 10 kcal/mole. Other investigators^{13–15} noted two competing reactions, the homomolecular exchange of gaseous oxygen with itself and the exchange of gaseous oxygen with the metal oxide layer. Johnson and O'Shea¹⁶ also observed a photochemical exchange due to 2357-Å radiation and a first-order dependence for the mercury-photosensitized reaction.

Experimental Section

The Reactors and Reactants. Two single-pulse shock tubes, 1 and 2 in. in diameter, were used in this study. Each could be pumped down to less than 5×10^{-5} Torr in about 0.5 hr, and had a leak rate of less than $0.1 \mu/\text{min}$. The smaller tube is of glass, similar to that used in our previous studies^{17–19} except that the vacuum system was completely reconstructed, the ball valve at the end block was removed, and the size of the damping tank was increased to 1000 in.³ The 2-in. diameter tube (Figure 1) is made of brass and scaled with respect to (d/L) to the satisfactorily operating 1-in. tube. The larger tube has an additional feature which was not used in the present study; a gas dynamically smooth rotating valve in the sample block may be closed to isolate a 15-in.³ terminal section of the test gas, such that all of it can be removed for analysis without incorporating the remaining sample.

Since data were taken with two different tubes, it was necessary to establish that they give mutually consistent results. For this purpose the well-known unimolecular dehydration



was measured over a 200° range in each tube; the measured conversion ratios in the two tubes agreed very well.

Incident shock speeds were obtained from measured time intervals between two Kistler quartz pressure transducers. Shock parameters were then calculated in the usual manner assuming no reaction in the incident and reflected shock regimes. Enthalpies were inserted as polynomials in the absolute temperature, with the total percentage of oxygen presumed to be at the natural isotope abundance ratio. Corrections for reaction during the cooling expansion period were estimated to be less than 10% and were not made. The diaphragm material was Mylar film, with thicknesses ranging from 0.25 to 2.0 mil. The driver gas was helium; $P_2:P_1$ ratios were in the 15–30 range; P_1 was between 40 and 200 Torr. Immediately after shock initiation a 25-ml sample was removed from the end block by opening a stopcock to a previously evacuated bulb.

Oxygen-36 gas was prepared by electrolysis of a degassed 1-g sample of 97.59 atom % ^{18}O enriched water (mostly $D_2^{18}O$) obtained from Yeda Research and Development Co., Ltd., Rehovoth, Israel. The water was made conductive by the addition of sodium metal of a weight sufficient to make the solution approximately 4 *M* in Na^+ , and placed in a small electrolytic cell.²⁰ The evolved gas was passed through a trap filled with platinized asbestos (room temperature) in an attempt to remove the hydrogen. It was then adsorbed onto activated charcoal cooled by liquid nitrogen. This served as a "pump" and reservoir to store the gas in a 1-l. bulb. When the temperature was slowly raised most of the coadsorbed water remained on the charcoal. The rest was removed by flowing the gas slowly past a liquid nitrogen cold finger. The $^{36}O_2$ gas produced by this procedure was analyzed mass spectrometrically and found to contain 92.0% $^{36}O_2$, 3.14% $^{32}O_2$, 0.79% $^{34}O_2$, 2.72% D_2 , and 1.33% HD.²¹ Quantitative analysis for H_2 could not be

(13) V. I. Gorgoraki, G. K. Boreskov, L. A. Kasatkina, and V. D. Sokolovskii, *Kinetics Catalysis (USSR)*, **5**, 100 (1964).

(14) L. A. Kasatkina and A. P. Zuev, *ibid.*, **6**, 413 (1965).

(15) Y. L. Sandler and D. D. Durigan, *J. Phys. Chem.*, **72**, 1051 (1968).

(16) W. H. Johnston and C. J. O'Shea, *J. Chem. Phys.*, **21**, 2080 (1953).

(17) A. Lifshitz, S. H. Bauer, and E. L. Resler, Jr., *ibid.*, **38**, 2056 (1963).

(18) A. Lifshitz, H. F. Carroll, and S. H. Bauer, *J. Am. Chem. Soc.*, **86**, 1488 (1964).

(19) A. Lifshitz, H. F. Carroll, and S. H. Bauer, *J. Chem. Phys.*, **39**, 1661 (1963).

(20) D. Samuel in "Oxygenases," O. Hayaishi, Ed., Academic Press, New York, N. Y., 1962.

(21) It is not clear why mass 32 was greater than mass 34. This may indicate the presence of a slight air leak, or incomplete degassing of the ^{18}O -enriched water.

Table I. Initial Oxygen Mole Fractions (x_{32} and x_{36}), Average Densities (ρ_0) (moles/l.) behind the Reflected Shocks, and Initial Oxygen:Argon²⁰ Ratios (a , b , x_0) for Each Data Set

Set	x_{32}	x_{36}	$\rho_0 \times 10$	$\rho_{Ar} \times 10$	$\rho(^{32}\text{O}_2 + ^{36}\text{O}_2) \times 10^3$	a^a	b^b	x_0^c
A	0.0177	0.00169	0.128	0.125	0.247	74.0	7.06	0.320
B	0.0177	0.00169	0.403	0.395	0.782	74.9	7.06	0.320
C	0.00569	0.000530	0.115	0.115	0.0715	24.0	2.24	0.104
D	0.00569	0.000530	0.432	0.428	0.268	24.0	2.24	0.104
E	0.0169	0.00169	0.119	0.117	0.221	73.3	7.07	0.323
F	0.0169	0.00169	0.454 ₅	0.446	0.845	74.3	7.07	0.323
G	0.00423	0.000403	0.120	0.119	0.0556	18.13	1.74	0.079
H	0.00423	0.000403	0.447	0.445	0.207	18.13	1.74	0.079

^a $a \equiv 10^3[\text{peak } (^{32}\text{O}_2)_i/\text{peak } (^{40}\text{Ar})]$. ^b $b = 10^3[\text{peak } (^{36}\text{O}_2)_i/\text{peak } (^{40}\text{Ar})]$. ^c $x_0 = 0.5 \times 10^3[\text{peak } (^{34}\text{O}_2)_i/\text{peak } (^{40}\text{Ar})]$.

performed due to the large mass spectrometer background at mass 2. However, there was much less H₂ in the sample than HD. At mass 22 (D₂¹⁸O) there was no peak; whatever trace of H₂¹⁸O that was present was masked by the (³⁶O₂²⁺) peak. The ³²O₂ used in this study was Matheson Research Grade, listed as 99.95%, with less than 400 ppm of N₂, 100 ppm of Ar, 50 ppm of H₂, and 100 ppm of both CO₂ and CO. The argon and helium were of Matheson High Purity Grade listed as 99.995%.

Isotopic Analysis. All analyses were made with a CEC 21-103 mass spectrometer. Ion currents were measured with a Cary No. 31 vibrating reed electrometer, the output of which was fed to a chart recorder. The ionizing voltage was kept at 70 eV and the current at 10 mA. Generally, the expansion chamber operated at about 50 μ total pressure, and the sample gas leaked into the ion source through a pinhole in a gold leaf septum. "Peak heights" were recorded by adjusting the ion accelerating voltage so that individual mass numbers remained focused on the collector for several moments. Under these conditions, the sensitivity to oxygen was about 0.00005%. Thus, even in the most dilute mixtures studied, extents of reaction as small as 5% could be measured. The argon m/e 20 peak height was used as an internal standard such that only ratios of (oxygen:argon 20) were used in calculating the exchange rate constants. Unfortunately, the ³⁶Ar masked the ³⁶O₂ peak so that analytical data were available only for ³⁴O₂ and ³²O₂. The oxygen-argon mixtures that were used in this study are listed in Table I. All were prepared in a high-vacuum glass line. The mixtures were stored in 12-l. glass bulbs before use. The pertinent shock parameters and analytical data are summarized in the Appendix.

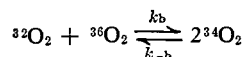
Reduction of the Data

The experimental parameters needed to deduce a mechanism are the partial orders for the various species, the overall activation energy, and the preexponential factor in the Arrhenius equation. The first step was to obtain the values α , β , and γ in the empirical relation

$$\text{rate} = k[^{32}\text{O}_2]^\alpha [^{36}\text{O}_2]^\beta [\text{Ar}]^\gamma \quad (1)$$

Ninety-eight shocks were run in two batches [Table I, A-D and E-H]. These were executed about 6 months apart and represent two independent determinations of the same parameters. Twelve shocks in set A were run in the 2-in. tube; all the others were run in the 1-in. tube.

The magnitudes of α , β , and γ were determined by two independent procedures. To allow for concentration changes during reaction, start with an approximate rate law for the reaction



The integrated bimolecular expression is

$$k_b = \frac{1}{\tau a + b + 2x_0} \ln \frac{ab - x_0^2}{ab - x_0^2 - (a + b + 2x_0)x} \quad (2)$$

where $a \equiv [^{32}\text{O}_2]_{\text{init}}$, $b \equiv [^{36}\text{O}_2]_{\text{init}}$, $2x_0 \equiv [^{34}\text{O}_2]_{\text{init}}$, $2x = [^{34}\text{O}_2]$ generated during reaction, $k_b = a$ bimolecular rate

constant, and $\tau =$ dwell time. Now define a pseudo-first-order rate constant

$$k_u \equiv \frac{1}{\tau} \ln \frac{ab - x_0^2}{ab - x_0^2 - (a + b + 2x_0)x} \quad (3)$$

Then $k_b = k_u/(a + b + 2x_0)$. By plotting $\log k_u$ vs. $1/T_5$ for different ratios of oxygen to argon, the total order, the argon partial order, and the partial order of the sum of the oxygen species ($[^{32}\text{O}_2] + [^{36}\text{O}_2]$) may be determined. The partial orders of the oxygen isotopes (α and β) were assumed to be equal. Since $(a + b) \gg 2x_0$, $k_b \approx k_u/(a + b)$ was used in the calculations. Figure 2 shows the individual plots and Table II lists the partial orders derived from them, as follows.

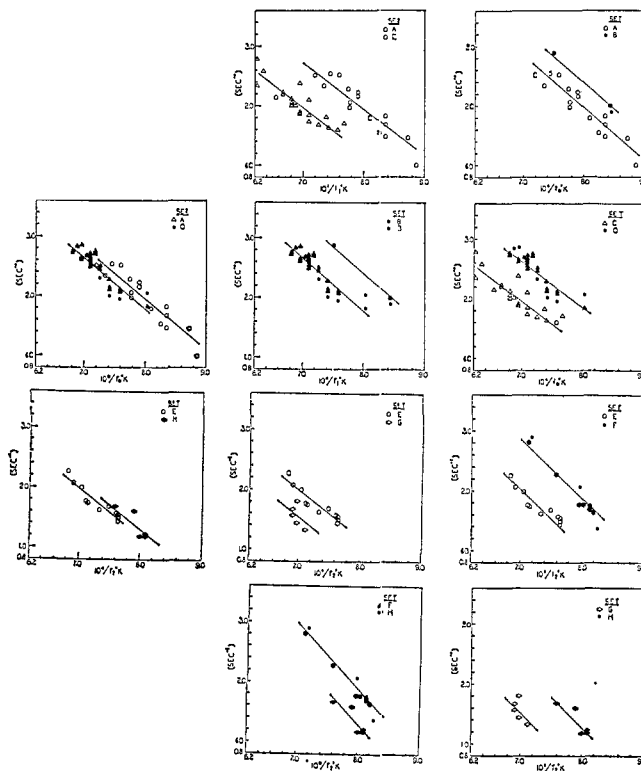


Figure 2. Plots of $\log k_u$ vs. $1/T_5$ for various combinations of data sets to determine partial and total orders. Ordinates are all $\log k_u$ (sec⁻¹).

If $(a + b)$ is increased by the factor ξ from one set of shocks to another, keeping $[\text{Ar}]$ constant, the oxygen partial order is given by

$$\Delta(\log k_u)/\log \xi = (\alpha' + \beta') \quad (4)$$

Table II. Order Parameters as Deduced from Different Combinations of Data Sets

Order	Data sets	$\Delta(\log k_u)$	Log (density ratio)	Order parameter
Argon	A-D	-0.17	0.534	$\gamma = -0.318$
Argon	E-H	0.11	0.580	$\gamma = 0.19$
Oxygen	A-C	0.76	0.539	$\alpha + \beta = 2.41$
Oxygen	B-D	0.62	0.465	$\alpha + \beta = 2.33$
Oxygen	E-G	0.46	0.599	$\alpha + \beta = 1.77$
Oxygen	F-H	0.59	0.610	$\alpha + \beta = 1.97$
Total	A-B	0.42	0.499	$\alpha + \beta + \gamma = 1.82$
Total	C-D	0.66	0.574	$\alpha + \beta + \gamma = 2.15$
Total	E-F	0.84	0.582	$\alpha + \beta + \gamma = 2.45$
Total	G-H	0.79	0.572	$\alpha + \beta + \gamma = 2.38$

Table III. Reactions and Rate Constants Used in the CAL Program to Compute O Atom Concentration

Reaction	Rate constant, $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1} \text{kcal}$	Reaction no., ref
$\text{O}_2 + \text{M} = 2\text{O} + \text{M}$	$k = 3.6 \times 10^{18} T^{-1} \exp(-118/RT)$	1, a
$\text{H}_2 + \text{M} = 2\text{H} + \text{M}$	$k = 2.23 \times 10^{12} T^{1/2} \exp(-92.6/RT)$	2, b
$\text{H}_2 + \text{O}_2 = 2\text{OH}$	$k = 2.51 \times 10^{12} \exp(-39/RT)$	3, c
$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	$k = 7.75 \times 10^{13} \exp(-14.45/RT)$	4, d
$\text{O} + \text{H}_2 = \text{OH} + \text{H}$	$k = 3.24 \times 10^{13} \exp(-10/RT)$	5, e
$\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	$k = 2.3 \times 10^{13} \exp(-5.15/RT)$	6, f
$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	$k = 2.0 \times 10^{15} \exp(0.87/RT)$	7, g
$\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$	$k = 1.55 \times 10^{12}$	8, h
$\text{H}_2\text{O} + \text{M} = \text{OH} + \text{H} + \text{M}$	$k = 5 \times 10^{14} \exp(-105/RT)$	9, i

^a D. L. Ripley and W. C. Gardiner, Jr., *J. Chem. Phys.*, **44**, 2285 (1966). ^b A. L. Meyerson and W. S. Watt, *ibid.*, **49**, 425 (1968). ^c Reference 1. ^d D. Gutman and G. L. Schott, *J. Chem. Phys.*, **46**, 4576 (1967). ^e Reference 4. ^f W. E. Wilson, Western States Section Meeting, The Combustion Institute, LaJolla, 1967; Report on the Establishment of Chemical Kinetics Tables, Chemical Propulsion Information Agency, April 1967. ^g D. Gutman, F. A. Hardwidge, F. A. Dougherty, and R. W. Lutz, submitted for publication. ^h W. E. Wilson and J. T. O'Donovan, *J. Chem. Phys.*, **47**, 5455 (1967). ⁱ H. A. Olschewski, J. Troe, and H. Gg. Wagner, 11th Internal Combustion Symposium, The Combustion Institute, Pittsburgh, Pa., 1967, p 155.

Since k_u is first order with respect to oxygen, $(\alpha + \beta) = (\alpha' + \beta' + 1)$. If the argon density is changed by a factor ζ from one set of shocks to another, keeping $(a + b)$ constant, the argon partial order follows from

$$\Delta(\log k_u)/\log \zeta = \gamma \quad (5)$$

To determine the total order, the total density is changed by a factor κ for two sets of shocks, keeping the mole fractions of all species fixed. Then

$$\Delta(\log k_u)/\log \kappa = (\alpha' + \beta' + \gamma') \quad (6)$$

where the total order is $(\alpha' + \beta' + \gamma' + 1)$. In Figure 2 the vertical separation between two lines on a $\log k_u$ vs. $1/T_5$ plot gives $\Delta(\log k_u)$. It is estimated by assigning a common slope to both lines and determining the distance between the intercepts on the $\log k_u$ axis.

Table II shows that the order parameters found in this manner for group I (data sets A-D) are not in good agreement with those of group II (data sets E-H).

A procedure for obtaining a more consistent set of values (and one in which we place greater reliance) is to use a least-squares regression of $1/T_5$ vs. $\log k$. (There is now adequate basis²² for treating $\log k_{\text{exp}}$ as the more precisely determined variable, and the reciprocal of the reflected shock temperature as the less precisely measured variable.) The rate constant was calculated for each group of data on the basis of the empirical relation (1). Here define $\text{rate} = 2x/\tau$; then $[\text{}^{32}\text{O}_2]_{\text{mean}} = (a - x)/2$, $[\text{}^{36}\text{O}_2]_{\text{mean}} = (b - x)/2$. Sequences of values of α , β , and γ were tested covering the range suggested by

(22) W. Tsang, *J. Chem. Phys.*, **46**, 2817 (1967), and previous publications by this author.

Table II. The criterion for selecting the best parameters was the minimum separation of Arrhenius lines for the different data sets within each group, as measured by the smallest standard deviation of the slope of the least-squares line. $\alpha = \beta = 1$ and $0 < \gamma < 0.25$ were found to give the smallest magnitude for that standard deviation for both groups of data.

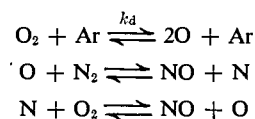
In addition to the empirical rate law 1, we also tested

$$\text{rate} = k([\text{}^{32}\text{O}_2] + [\text{}^{36}\text{O}_2])^2[\text{Ar}]^\gamma \quad (7)$$

For both groups taken together, $0.0 < \gamma < 0.20$, eq 7 is indistinguishable from (1) with $\alpha = \beta = 1$. For neither rate expression is it possible to establish more precisely the value of γ ; it ranges between 0 and 0.2.

Effects of Impurities on the Exchange Rate

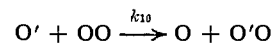
A Possible Nitrogen Impurity. Two mechanisms have been proposed, which differ in the initiation step, by which nitrogen and oxygen react to form NO. Reaction conditions determine which initiation step dominates in producing oxygen atoms. The following rough calculation demonstrates that under the conditions of these experiments the oxygen atoms produced by such chains could not influence the observed isotope exchange rates. Consider first



$k_d = 3.6 \times 10^{18} T^{-1} \exp(118,000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ (reaction 1 in Table III). At 1400°K and $P_1 = 16 \text{ cm}$, with 2% oxygen and 2% nitrogen (a vast overestimate), the concentration of O atoms after 1 msec may be estimated from

$$[\text{O}] = 2k_d[\text{O}_2][\text{Ar}]\Delta t = 9.16 \times 10^{-17} \text{ mole cm}^{-3}$$

If atom switching is assumed to take place *via* the reaction²³



with $k_{10} = 10^{14} \exp(-8000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, the total exchange) due to this process is

$$\begin{aligned} \Delta(\text{exchange}) &= k_{10}([\text{O}'][\text{OO}] + [\text{O}][\text{O}'\text{O}'])\Delta t = \\ &1.5 \times 10^{-13} \text{ mole cm}^{-3}. \end{aligned}$$

(23) S. H. Bauer and S. C. Tsang, *Phys. Fluids*, **6**, 182 (1963).

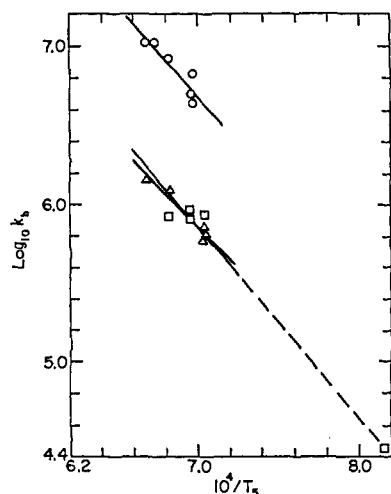
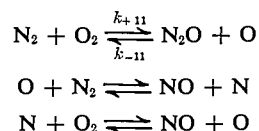


Figure 3. Experimental values for $\log k_b$ vs. $1/T_s$, showing the influence of added deuterium: \circ , 0.014% D_2 added; \square , 0.0018% D_2 added; \triangle , no D_2 added.

The second possibility is



where $k_{-11} = 6.3 \cdot 10^{14} \exp(-26,705/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$,²⁴ and k_{11} may be estimated from this value and the known equilibrium constant. This gives $k_{11} = 3.28 \cdot 10^{25} \exp(-107,800/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, or at 1400°K, $k_{11} = 0.00496 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. Again assuming a mixture which is 2% O_2 , 2% N_2 , and 96% argon, $[O] = k_{11}[O_2][N_2]\Delta t = 4.76 \cdot 10^{-18} \text{ mole cm}^{-3}$ after 1 msec. Exchange due to atom switching is $\Delta(\text{exchange}) = 5.96 \cdot 10^{-15} \text{ mole cm}^{-3}$. Under the conditions of the above calculations, the observed exchange is about $7 \cdot 10^{-7} \text{ mole cm}^{-3}$. Clearly, the atomic displacement process alone does not account for the observed exchange rates.

Effect of the Deuterium Impurity. The $^{36}O_2$ produced by electrolysis contained about 4% of a mixture of D_2 , HD, and H_2 , so that the oxygen-argon mixtures used in the shock experiments contained 0.002% D_2 in the 0.5% $^{32}O_2$ -0.05% $^{36}O_2$ mixture and 0.0068% D_2 in the 1.7% $^{32}O_2$ -0.17% $^{36}O_2$ mixture. (The isotopic hydrogen will be referred to as D_2 for convenience.) In order to determine if these levels of D_2 could affect the exchange kinetics via the hydrogen-oxygen combustion, both experimental and computer studies were carried out.

Sixteen shocks were made in 1 day with three different mixtures. Mixture 1 (runs 1-5) contained 0.5% $^{32}O_2$, 0.05% $^{36}O_2$, and 0.002% D_2 . Mixture 2 (runs 6-10) contained 0.5% $^{32}O_2$, 0.05% $^{36}O_2$, and 0.0038% D_2 . Mixture 3 (runs 11-16) contained 0.417% $^{32}O_2$, 0.0398% $^{36}O_2$, and 0.016% D_2 . The observed bimolecular rate constants for exchange are plotted in Figure 3. It is evident that doubling the D_2 concentration (as initially present) had no noticeable effect on the rate of exchange, but an eightfold increase in D_2 increased the rate by about a factor of 6. These experiments show that the small amount of D_2 present in the $^{36}O_2$ has no effect on the rate of exchange.

(24) H. Henrici and S. H. Bauer, *J. Chem. Phys.*, **50**, 1333 (1969).

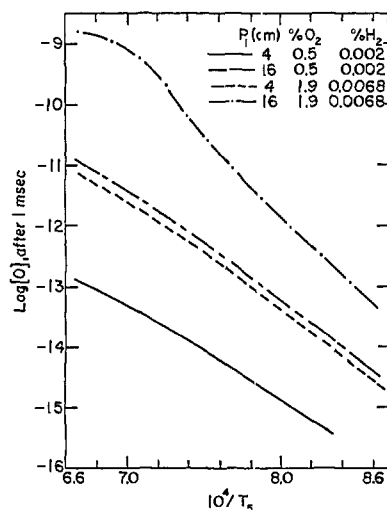
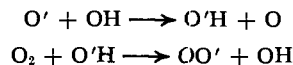


Figure 4. Calculated oxygen atom concentrations, after 1 msec, vs. $1/T_s$.

The following computer study was then undertaken to check whether the calculated oxygen atom concentrations for the various mixtures could account for the above observations. The program used was obtained from Cornell Aeronautical Laboratory.²⁵ It calculates the concentration of each species as a function of time behind the incident shock, the instantaneous rate of production of each species from each reaction, and the degree of nonequilibrium of each reaction. Table III lists the nine reactions believed to be dominant in the 1100-1500°K temperature range, along with acceptable literature values for the corresponding rate constants. H_2 and $^{32}O_2$ were the only isotopes considered in these calculations. Enthalpies and free energies were taken from Bird, Duff, and Schott,^{26a} except those for HO_2 which were taken from the "JANAF Thermochemical Tables."^{26b} The amount of exchange was calculated using the oxygen atom concentration present at the end of 1 msec, as was done in the above discussion on the effect of nitrogen. This is a rough but adequate approximation.

The O atom concentrations present at 1 msec calculated in this manner are listed in the seventh column of Table IV. Figure 4 shows that the oxygen atom concentration grows exponentially with temperature. This is expected, except for the shape of the topmost curve, for which there is no obvious explanation. Also listed in Table IV are the exchanges observed and the corresponding fractions of exchange calculated to be due to atom displacement. Two other reactions could also contribute to exchange



The first would be slow due to the low concentration of reactants and the second would at most double the estimated exchange calculated as due to O atoms.

(25) L. J. Garr, P. V. Marrone, W. W. Joss, and M. J. Williams, "Inviscid, Nonequilibrium Flow Behind Bow and Normal Shock Waves," Part III, The Revised Normal Shock Program, CAL Report No. QM-1626-A-12(III), Oct 1966.

(26) (a) P. F. Bird, R. E. Duff, and G. L. Schott, "Hug, A Fortran-FAP Code for Computing Normal Shock and Detonation Wave Parameters in Gases," Los Alamos Scientific Laboratory Report LA-2980, 1964; (b) "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Co., Midland, Mich., 1961.

Table IV. Maximum Fraction of Exchange Due to Oxygen Atoms, Produced in Mixtures of Oxygen and Hydrogen^a

T_5	P_1 , Torr	ρ_5 , $\times 10^5$	% O ₂	% H ₂	[O ₂], $\times 10^8$	[O], 1 msec, $\times 10^{14}$	k_a , $\times 10^{14}$	Exchange, calcd $\times 10^{10}$, in 1 msec	Exchange, obsd $\times 10^{10}$, Gp I	Fraction due to O atoms	Exchange, obsd $\times 10^{10}$, Gp II	Fraction due to O atoms
1404	40	1.29	0.5	0.002	6.45	2.94	6.4	0.0243	8.06	0.003	2.42	0.01
1404	160	5.1	0.5	0.002	25.8	256	6.4	8.45	194	0.0435		
1404	40	1.29	1.9	0.0068	24.5	158	6.4	4.95	55.5	0.045	11.4	0.43
1404	160	5.1	1.9	0.0068	98.0	57200	6.4	7180			799	9.6(*)
1404	40	1.29	0.5	0.004	6.45	11.8	6.4	0.0975	6.42	0.0152		
1404	40	1.29	0.5	0.014	6.45	205	6.4	1.7	23.5	0.0725		
1295	40	1.29	0.5	0.002	6.45	0.447	4.06	0.00234	11.8	0.0002		
1295	160	5.1	0.5	0.002	25.8	24.9	4.06	0.522			21.2	0.0246
1295	40	1.29	1.9	0.0068	24.5	160	4.06	0.318	65.7	0.00242	5.52	0.159
1295	160	5.1	1.9	0.0068	98.0	741	4.06	59.0	800	0.074	290	0.204

^a Under reflected shock conditions. Based on [O] as calculated with the CAL Program. Densities and concentrations are in moles cm⁻³; rate constants in cm³ mole⁻¹ sec⁻¹. Runs with 0.004 and 0.014% H₂ are listed in the Gp I column, but these runs were made separately, as described in the text.

Table V. Summary of Four-Center Exchange Reactions, $d[AX]/dt = k[AB]^{\alpha}[X_2]^{\beta}[Ar]^{\gamma}$

AB	X ₂	α	β	γ	E_a , kcal/mole	$A(T^{1/2})$, moles/l.	Ref
H ₂	D ₂	0.50	0.80	0.70	42.26 ± 2.1	10 ^{9.94} T ^{1/2}	6
HD	HD	0.71	0.71	0.58	35.9 ± 2	10 ^{9.39}	9
HSH	D ₂	0.45	1.02	0.53	52.8 ± 2	10 ^{10.42} T ^{1/2}	8
HNH ₂	D ₂	0.50	1.05	0.45	38 ± 3	10 ⁸ T ^{1/2}	5
HCH ₃	D ₂	0.3	1.1	0.6	52.00 ± 2.2	10 ^{9.04} T ^{1/2}	7
²⁸ N ₂	³⁰ N ₂	$\alpha + \beta = 1$		1.0	116 ± 5	10 ^{10.82}	10
¹³ C ¹² O	¹² C ¹⁸ O	$\alpha + \beta = 1.45$		0.6	76 ± 2	10 ^{11.36}	11

Except for one case, the calculated amount of exchange due to oxygen atoms was considerably less than that observed. The run with 0.014% D₂ added gave only 7% exchange due to oxygen atoms, although experimentally the added D₂ increased the exchange rate by a factor of 6. We have no explanation for the case with nine times the experimental rate (marked with an asterisk). It proved to be a single nonreproducible experiment.

As a check on the operation of the computer program, a calculation was made at 1600°K using 4% H₂-2% O₂ in argon with $P_1 = 10$ cm. These were the conditions used by Duff as quoted in Schott and Kinsey's Figure 2.²⁷ The results of the CAL program showed a slight overshoot in the OH, peaking about 30 μ sec behind the incident shock while Duff's OH concentration peaked at about 25 μ sec. He found an exponential growth of OH with time up to the peak, while the CAL program showed an almost linear growth of OH, except for the first 5 μ sec. However, the rate constants used in the present study are quite different from those of Duff. In fact, a plot of [OH] vs. time from the CAL program has a shape similar to the experimental absorption record given by Schott and Kinsey, although no quantitative comparison could be made. Thus, no obvious error was found in the CAL program. The experiment in which D₂ was added to the oxygen may be relied upon as demonstrating that the D₂ present as an impurity in the oxygen had no significant effect on the observed rate.

Discussion

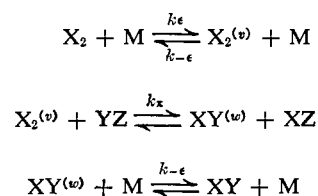
The oxygen-exchange rates measured in this investigation are compatible equally well with empirical rate expressions 1 and 7. For either case, the partial order for argon was found to be less than 0.25, and probably

(27) G. L. Schott and J. L. Kinsey, *J. Chem. Phys.*, **29**, 1175 (1958).

it is close to zero. The reaction is clearly second order with respect to total oxygen. In the following discussion the dependence on argon concentration will be assumed to be zero.²⁸ If one accepts a total order of 2.2 he is forced to postulate a very complex mechanism to account for the data. Of course, one could terminate this discussion by describing the atom switching process as a direct bimolecular four-center step. However, the activation energy is too low [(38.4-44.2) kcal/mole is only $\frac{1}{3}D_0(O-O)$. Noyes²⁹ predicted $E_a \approx 51$ kcal/mole]; hence this simple postulate is suspect.

In the numerous shock tube investigations of homogeneous isotope exchange reactions, summarized in Table V, the only mechanism which is compatible with all the data involves vibrational excitation. The key observation is the presence of an Ar dependence, with an order of 0.5-1.0. By extension we argue that the oxygen exchange also follows a vibrational excitation mechanism, and that the absence of an Ar dependence is due to an unresolved problem in the O₂ vibrational excitation processes by Ar relative to O₂ colliders.

In the simplest formulation of a vibrational excitation mechanism, a two-level model is utilized.



(28) We have also considered the plausible expression for the empirical rate $d(34)/dt = k[32]^{0.9}[36]^{0.9}[Ar]^{0.2}$. This led to preexponential factors about one-third as large as those listed in Table VI, and thus are somewhat more appealing. However, the analysis then gets more involved.

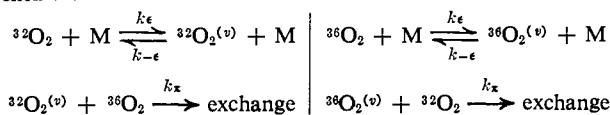
(29) R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4318 (1966).

The steady-state concentration of $X_2^{(v)}$ is given by

$$[X_2^{(v)}]_{ss} = \frac{k_e[X_2][M]}{k_{-e}[M] + k_x[YZ]} \quad (8)$$

(k_{-x} is neglected for the case of low conversions.) On applying the above formalism to the oxygen exchange, the reaction scheme is as shown in Scheme I.

Scheme I



Let the subscript 1 refer to argon and subscript 2 refer to oxygen. Since

$$\text{rate} \equiv \frac{1}{2} \frac{d[{}^{34}\text{O}_2]}{dt} = k_x[{}^{32}\text{O}_2^{(v)}][{}^{36}\text{O}_2] + k_x[{}^{36}\text{O}_2^{(v)}][{}^{32}\text{O}_2] \quad (9)$$

on substituting the steady-state values for the vibrationally excited species

$$\text{rate} = \frac{k_x(k_{e1}[M_1] + k_{e2}[M_2])}{k_{-e1}[M_1] + k_{-e2}[M_2]} [{}^{32}\text{O}_2][{}^{36}\text{O}_2](\Lambda_{36} + \Lambda_{32}) \quad (10)$$

where

$$\Lambda_{36}^{-1} = 1 + \frac{k_x[{}^{36}\text{O}_2]}{k_{-e1}[M_1] + k_{-e2}[M_2]}$$

$$\Lambda_{32}^{-1} = 1 + \frac{k_x[{}^{32}\text{O}_2]}{k_{-e1}[M_1] + k_{-e2}[M_2]}$$

Equation 10 may be reduced to a simpler form by introducing one of several limiting assumptions.

Assumption I. $k_{e1}[M_1] \ll k_{e2}[M_2]$. Therefore, $k_{-e1}[M_1] \ll k_{-e2}[M_2]$. Now, if in addition

$$\frac{k_x[{}^{36}\text{O}_2]}{k_{-e2}[M_2]} \gg 1 \quad \text{and} \quad \frac{k_x[{}^{32}\text{O}_2]}{k_{-e2}[M_2]} \gg 1 \quad (\text{Ia})$$

$$\text{rate} \approx k_{e2}([{}^{32}\text{O}_2] + [{}^{36}\text{O}_2])^2 \quad (11)$$

$$\frac{k_x[{}^{36}\text{O}_2]}{k_{-e2}[M_2]} \ll 1 \quad \text{and} \quad \frac{k_x[{}^{32}\text{O}_2]}{k_{-e2}[M_2]} \ll 1 \quad (\text{Ib})$$

it follows that

$$\text{rate} = \frac{2k_x k_{e2}}{k_{-e2}} [{}^{32}\text{O}_2][{}^{36}\text{O}_2] \quad (12)$$

Although formally this model appears to be equivalent to the conventional four-center bimolecular exchange step, quantitatively it differs from it in that here only vibrational excitation is counted.

Assumption II. $k_{e1}[M_1] \gg k_{e2}[M_2]$; therefore, $k_{-e1}[M_1] \gg k_{-e2}[M_2]$. If in addition

$$\frac{k_x[{}^{36}\text{O}_2]}{k_{-e1}[M_1]} \gg 1 \quad \text{and} \quad \frac{k_x[{}^{32}\text{O}_2]}{k_{-e1}[M_1]} \gg 1 \quad (\text{IIa})$$

$$\text{rate} = k_{e1}([{}^{32}\text{O}_2] + [{}^{36}\text{O}_2])[M_1] \quad (13)$$

$$\frac{k_x[{}^{36}\text{O}_2]}{k_{-e1}[M_1]} \ll 1 \quad \text{and} \quad \frac{k_x[{}^{32}\text{O}_2]}{k_{-e1}[M_1]} \ll 1 \quad (\text{IIb})$$

$$\text{rate} = \frac{2k_x k_{e1}}{k_{-e1}} [{}^{32}\text{O}_2][{}^{36}\text{O}_2] \quad (14)$$

(Note the comment following (Ib)).

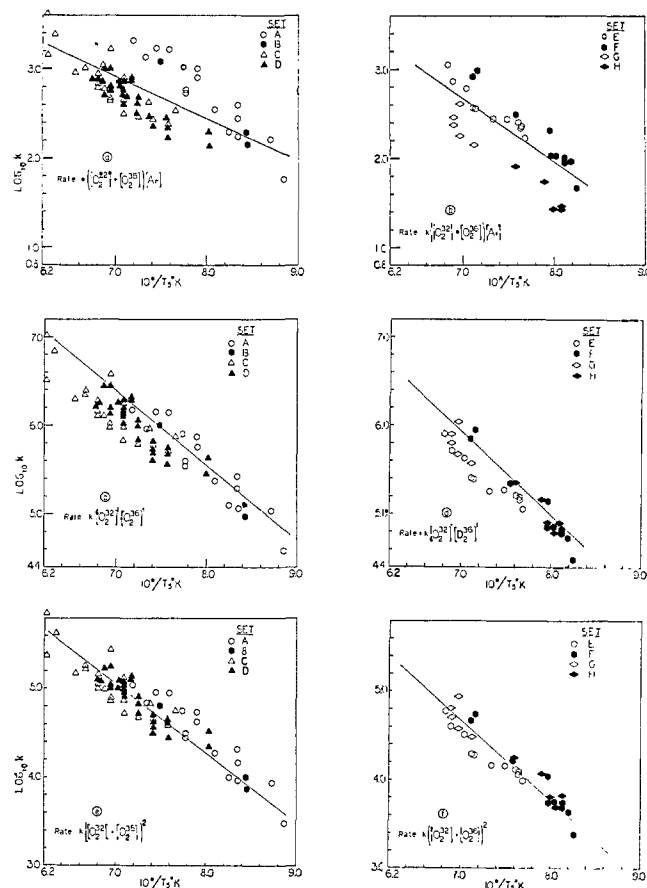


Figure 5. Exchange rate data reduced on the basis of alternate assumptions—plots of $\log k_b$ vs. $1/T_5$.

Assumption IIa leads to an argon order of unity which does not agree with experiment. This is underscored in Figure 5a,b which demonstrate that the scatter in the data is large when reduced according to expression 13. Assumptions Ib and IIb lead to similar bimolecular rate expressions. As shown in Figure 5c,d, the rate data reduced according to expression 11 show a small scatter about the least-squares line. Assumption Ia yields rate expression 7. In Figure 5e,f the points fit as well as they do for assumptions Ib and IIb. The overall rate constants (preexponential terms and activation energies) as evaluated by least squares, according to eq 11–14, are listed in Table VI. The magnitude of σ_E measures the quality

Table VI. Arrhenius Factors for Rate Constants Deduced from Exchange Data According to the Assumptions Indicated^a

Set	Assumption	A , $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$	E , kcal/mole	σ_E
A–D	IIa	$\approx 5 \times 10^{10}$	~ 24	~ 2.8
	Ib and IIb	1.86×10^{15}	38.45	2.03
	Ia	3.48×10^{13}	35.85	1.72
E–H	IIa	$\approx 8 \times 10^{12}$	~ 40	~ 4.7
	Ib and IIb	5.50×10^{15}	44.25	2.58
	Ia	1.09×10^{14}	41.65	2.52

^a Regression treats $1/T_5$ as the less precise variable

of the fit, expressed as the standard deviation of the activation energy, for the best straight line through the points; IIa is clearly not acceptable.

Analysis of the Vibrational Excitation Mechanism

For a multistate model, the equation which describes the time rate of change of $O_2^{(v)}$ (in the critical vibrational level) is

$$\frac{d[O_2^v]}{dt} = \eta_{v-1,v}[O_2^{v-1}][M] + \eta_{v+1,v}[O_2^{v+1}][M] - \eta_{v,v+1}[O_2^v][M] - \eta_{v,v-1}[O_2^v][M] - k_x[O_2^v][O_2] \quad (15)$$

where $\eta_{i,j}$ is the probability for transition (in $cm^3 \text{ mole}^{-1} \text{ sec}^{-1}$) from the i th to the j th level. Because the population of the $(v+1)$ level is low, not only because of the Boltzmann factor but also because of depletion, transitions from this to the lower level need not be considered. Furthermore, $\eta_{v,v-1}$ is considerably larger than $\eta_{v,v+1}$ because of the Boltzmann factor. On solving eq 15 for $[O_2^v]$

$$[O_2^v] = \frac{B}{A}(1 - e^{-At}) \quad (16)$$

where

$$B = \eta_{v-1,v}[O_2^{v-1}][M] \quad (17)$$

$$A = \eta_{v,v-1}[M] + k_x[O_2]$$

For comparison, the steady-state expression for $[O_2^v] = B/A$. An estimate of the magnitude of A follows from $\eta_{v,v-1} > 10^9$ (justified below), $[M] \approx 10^{-5}$, $k_x > 10^{11}$, and $[O_2] \approx 10^{-7}$. Therefore, $A = 10^4$ – 10^5 and $e^{-At} \ll 1$ for t greater than 100 μsec . Typical reaction times in the present study were about 1000 μsec . Hence the steady-state approximation for $[O_2^v]$ is valid for at least 90% of the reaction period and will be used in the subsequent calculations, together with the $[O_2^{v-1}]_{\text{equil}}$, where that is appropriate. Further reduction of eq 16 depends on the limiting assumptions which are introduced.

Assumption Ia. If conditions are such that $k_x[O_2] \gg k_{-v}[M_2]$, then $A = k_x[O_2]$, and for steady state

$$k_x[O_2^v][O_2] \approx \eta_{v-1,v}[O_2^{v-1}][M_2] \quad (18)$$

Then the rate of exchange of oxygen in the v th level is equal to the rate of filling of that level from the $(v-1)$ th level. The nitrogen isotope exchange¹⁰ rate was accounted for in the same manner. To a first approximation one may estimate $[O_2^{v-1}]$ as being close to its equilibrium value, since only the v th and higher levels are presumed to be significantly depopulated by the exchange reaction. Thus

$$[O_2^{v-1}] = \exp(-E_{v-1}/RT)(1 - e^{-\theta/T})[O_2]$$

wherein the harmonic oscillator limit was used to evaluate the partition function. E_{v-1} is the energy of the $(v-1)$ level above $v=0$ and $\theta = (E_1 - E_0)/k = h\nu_{10}/k$ is the characteristic temperature for the first vibrational transition.

For an anharmonic oscillator, $\eta_{v-1,v} = \omega_v v \eta_{0,1}$, with $\omega_v > 1$, a parameter which depends on the degree of anharmonicity.

$$\eta_{v-1,v}[O_2^{v-1}][O_2] = \omega_v v \eta_{0,1}(1 - e^{-\theta/T}) \exp(-E_{v-1}/RT)[O_2]^2 \quad (19)$$

On inserting

$$\eta_{0,1} = \eta_{1,0} e^{-\theta/T} \quad \text{and} \quad \frac{RT}{P\tau} = \eta_{1,0}(1 - e^{-\theta/T}) \quad (20)$$

one finds

$$\eta_{v-1,v}[O_2^{v-1}][O_2] = \omega_v v \left(\frac{RT}{P\tau}\right) e^{-\theta/T} \times \exp(-E_{v-1}/RT)[O_2]^2 \quad (21)$$

The temperature dependence of $RT/P\tau$ may be obtained empirically^{6a,10} from measurements of O_2 - O_2 vibrational relaxation.³⁰ Over the 1100–1500°K temperature range

$$\frac{RT}{P\tau} = 4.37 \times 10^{11} \exp(-12,100/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad (22)$$

Also, the magnitude of the anharmonicity factor, ω_v , may be estimated by means of the empirical equation developed by Millikan and White^{30a} (their eq 3b), which expresses vibrational relaxation times in terms of the temperature, the reduced mass of the colliding pair, and the oscillator's characteristic frequency. Since the effect of anharmonicity is to increase the transition probability, the ω_v factor is estimated from the ratio of relaxation times for equivalent oscillators with a level spacing corresponding to the $(v-1) \leftrightarrow v$ separation, as present in the anharmonic oscillator. Thus

$$\omega_v = \frac{P\tau}{P\tau_{(h)}} \frac{e^{\theta/T} - 1}{e^{\theta_{v-1}/T} - 1} \quad (23)$$

where $\tau_{(h)}$ is the empirical relaxation time calculated according to Millikan and White's 3b for the characteristic temperature $\theta_{v-1} = (E_v - E_{v-1})/k$.

Under assumption Ia, the experimental exchange rate constant is identified with the right member of eq 21, and with the rate constant k_{e2} of eq 11 for the two-state model. Thus, the preexponential factor is $(4.37 \times 10^{11} \omega_v v) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, and the activation energy is $(E_{v-1} + R\theta + 12.1) \text{ kcal/mole}$. Setting the latter equal to the experimental E permits us to identify the critical level v , and thus to estimate magnitudes for the preexponential factor. These are listed in Table VII. Since the data in groups I and II gave

Table VII. Values Used to Calculate the Preexponential Factor of k_{e2} ^a

Gp	E_{v-1} , kcal/mole	v	$P\tau$, atm sec	$(e^{\theta_{v-1}/T} - 1)$	ω_v	A_{calcd} , $\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$
I	19.30	5	2.02×10^{-5}	4.03	2.24	4.90×10^{12}
II	25.10	6	1.70×10^{-5}	3.90	2.75	7.20×10^{12}

^a $P\tau = 3.98 \times 10^{-5} \text{ atm sec}$, and $(e^{\theta/T} - 1) = 4.58$.

different rate constants for exchange, separate calculations were made for each group. The magnitudes of v were found by comparing the deduced E_{v-1} with term values for the vibrational levels

$$E_v = 1580.361hc(v + 1/2) + 12.0730hc(v + 1/2)^2 + 0.0546(v + 1/2)^3 \quad (24)$$

For model Ia there is acceptable agreement between the estimated values of A (Table VII) and the experimental

(30) (a) R. C. Millikan and D. R. White, *J. Chem. Phys.*, **39**, 3209 (1963); (b) R. C. Millikan, "Molecular Relaxation Processes," Special Publication No. 20, The Chemical Society, London, 1966, pp 219–233; (c) A. I. Osipov and N. A. Generalov, *Fiz. Goreniya Vzryva*, **2**, 83 (1966); (d) S. L. Thompson, *J. Chem. Phys.*, **49**, 3400 (1968).

values listed in Table VI. The experimental result is 7.1 higher than the corresponding calculated value for group I while for group II it is 15.2 higher.

There is also an internal consistency check. Since assumption Ia requires that $k_x/k_{-e2} \gg [M_2]/[^{36}\text{O}_2]$ and $k_x/k_{-e2} \gg [M_2]/[^{32}\text{O}_2]$, it follows that $k_x/k_{-e2} > 10$. Now k_{-e2} may be estimated from the expression for the rate of deexcitation from the v th level to the $(v-1)$ th level.

$$\text{rate}(v \rightarrow v-1) = \eta_{v,v-1}[\text{O}_2^v][\text{O}_2] = \eta_{v-1,v} \times \exp(\theta_{v-1}/T)[\text{O}_2^v][\text{O}_2] \quad (25)$$

so that

$$k_{-e2} = (RT/P_T) \frac{\omega_v \exp[(\theta_{v-1} - \theta)/T]}{(1 - e^{-\theta/T})} \approx 1.22 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad (26)$$

for $\text{O}_2\text{-O}_2$ collisions, based on our exchange rates (group II) at 1300°K (group I gives a smaller value of k_{-e2}). Hence, k_x must be greater than $1.33 \times 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. This is entirely consistent with reasonable collision cross sections. However, a difficulty does remain in that under assumption Ia, $k_{e1}[\text{Ar}] \ll k_{e2}[\text{O}_2]$, or that $k_{e1}/k_{e2} < 1/200$. This is contradicted by the reported values: $P_T(\text{O}_2\text{-O}_2) \approx 0.1P_T(\text{O}_2\text{-Ar})$.³⁰ One may raise the question whether the measured relaxation times for $\text{O}_2\text{-Ar}$ collisions may have been accidentally lowered by about a factor of 10 by the presence of hydrocarbon impurities. The most careful experimental work was done with pure O_2 and indeed these relaxation times are quantitatively consistent with our kinetic data, as demonstrated above.

Assumption Ib. Here it is necessary that $k_x[\text{O}_2] \ll k_{-e2}[\text{M}_2]$ as well as $k_{e1}[\text{Ar}] \ll k_{e2}[\text{O}_2]$ which, as for Ia, is not consistent with the reported relative vibrational relaxation times. Also, since $k_{-e2} \approx 10k_{-e1}$ and $k/k_{-e2} \approx 10^3$ (see below), neither does it satisfy the condition $k_x/k_{-e2} \ll 10$.

Assumption Iib. This limiting condition requires that $k_{e1}[\text{Ar}] \gg k_{e2}[\text{O}_2]$ and thus is in agreement with the published relative vibrational relaxation times. It also requires that $k_x[\text{O}_2] \ll k_{-e1}[\text{Ar}]$; that is, no significant departure from equilibrium of the v th vibrational level due to reaction, which is a stronger condition than the steady state assumption, in that

$$[\text{O}_2^v]_{\text{equil}} = \exp(-E_v/RT)(1 - e^{-\theta/T})[\text{O}_2] \quad (27)$$

Since the exchange step is now rate limiting

$$\text{rate} = 2k_x \exp(-E_v/RT)(1 - e^{-\theta/T})[^{32}\text{O}_2][^{36}\text{O}_2] \quad (28)$$

The overall experimental rate constant k_b must now be identified with the two-level model (eq 14) and with the above

$$k_b = A \exp(-E/RT) \longleftrightarrow \frac{2k_x k_{e1}}{k_{-e1}} = 2k_x \exp(-E_v/RT)(1 - e^{-\theta/T}) \quad (29)$$

The term $(1 - e^{-\theta/T})$ is only weakly temperature dependent, as is k_x , so that the experimental activation energy E is essentially equivalent to E_v . Then

$$k_x = \frac{k_b}{2(1 - e^{-\theta/T})e^{-E_v/RT}} = \frac{A}{2(1 - e^{-\theta/T})} \quad (30)$$

At 1300°K, $2(1 - e^{-\theta/T}) = 1.64$. For group I, $A = 1.86 \times 10^{15} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ and $k_x = 1.13 \times 10^{15} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. For group II, $A = 5.50 \times 10^{15} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ and $k_x = 3.35 \times 10^{15} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. Since, k_x can be as large as a collision frequency, these numbers are not unacceptable. However, the following difficulty remains.

An estimate of k_{-e1} and ω_v can be made here, as has been done for Ia. In this case, the critical level $v = 9$ for group I and $v = 10$ for group II. For level 9, $\omega_v = 4.85$, and for level 10, $\omega_v = 5.22$. Thus $k_{-e1}(\text{group I}) = 3.60 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ and $k_{-e1}(\text{group II}) = 4.12 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. Therefore

$$\frac{k_x}{k_{-e1}} = \frac{1.13 \times 10^{15}}{3.60 \times 10^{11}} = 3.15 \times 10^3 \quad (\text{group I}) \quad (31a)$$

and

$$\frac{k_x}{k_{-e1}} = \frac{3.35 \times 10^{15}}{4.12 \times 10^{11}} = 8.15 \times 10^3 \quad (\text{group II}) \quad (31b)$$

Since $[\text{Ar}]/[^{36}\text{O}_2] \approx 200\text{-}2000$ and $[\text{Ar}]/[^{32}\text{O}_2] \approx 50\text{-}200$, the condition $k_x/k_{-e1} < [\text{Ar}]/[\text{O}_2]$ is not satisfied.

For the $^{32}\text{O}_2\text{-}^{36}\text{O}_2$ four-center exchange, attainment of complete consistency has proved illusive. It is possible that factors other than vibrational excitation enter into the mechanism. As indicated in the introduction, oxygen differs from the other diatomic molecules for which exchange reactions have been studied (CO , N_2 , H_2) in that it has a $^3\Sigma_g^-$ ground state, and it forms O_4 dimers at sufficiently high densities. Lewis^{31a} proposed that the dimerization of oxygen in liquid oxygen accounts for the observed decrease in paramagnetic susceptibility on liquefaction of oxygen-nitrogen mixtures. Wulf^{31b} identified some bands in gaseous oxygen spectra as being due to O_4 . Herzberg³² cites additional references to spectroscopic studies. Oxygen also differs from N_2 , CO , and H_2 , in that it has low-lying electronic states: the $^1\Delta_g$ state is 22.6 kcal/mole and the $^1\Sigma_g^+$ lies 37.6 kcal/mole above the ground $^3\Sigma_g^-$ state. On energy requirements alone, the $^1\Delta_g$, which has its zero vibrational level just below the fifth vibrational level of the $^3\Sigma_g^-$, might be involved in the exchange reaction. However, the transition probability of the $^1\Delta_g \rightarrow ^3\Sigma_g^-$ transition is extremely small, being about 10^{-9} of an ordinary electric dipole transition.³³ No information about the transition probability during collisional excitation of oxygen to the $^1\Delta_g$ state is available, and at present it appears doubtful that the $^1\Delta_g$ electronic state plays any part in the exchange reaction.

With regard to vibrational relaxation times, one should anticipate some slowing down of the attainment of vibrational equilibrium for $^{32}\text{O}_2$ in the presence of $^{36}\text{O}_2$ due to the slightly exothermic pumping reaction, $^{32}\text{O}_2^{(v)} + ^{36}\text{O}_2^{(w)} \rightarrow ^{32}\text{O}_2^{(v-1)} + ^{36}\text{O}_2^{(w+1)}$, but this factor is probably negligible. Finally one may question the effect of impurities on the relaxation times of the mixtures used in these experiments. Assuming that the $\text{O}_2\text{-D}_2$ relaxation efficiency is about the same as that of $\text{O}_2\text{-H}_2$, for a 98% Ar, 2% O_2 , and 0.0068%

(31) (a) G. N. Lewis, *J. Am. Chem. Soc.*, **46**, 2027 (1924); (b) O. R. Wulf, *Proc. Nat. Acad. Sci. U. S.*, **14**, 609 (1928).

(32) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950, pp 280, 465, 484.

(33) Reference 32, pp 278-279.

Table VIII. Input and Bimolecular Rate Constants (l. mole⁻¹ sec⁻¹) for Set A-H^a

No.	P ₁	T _s	ρ _s /ρ ₁	ρ _s	x	Log k _b τ, msec	No.	P ₁	T _s	ρ _s /ρ ₁	ρ _s	x	Log k _b τ, msec		
1	4.04	1266	5.22	0.0114	1.767	5.884	1.90	50	15.30	1410	5.39	0.0436	0.686	6.163	1.04
2	4.04	1317	5.35	0.0118	3.087	6.160	1.98	51	13.62	1455	5.48	0.0395	1.011	6.450	0.99
3	4.86	1197	5.02	0.0132	0.356	5.069	1.90	52	16.00	1245	5.00	0.0423	0.256	5.643	1.16
4	4.84	1197	5.02	0.0132	0.593	5.281	1.98	53	15.29	1410	5.39	0.0439	0.666	6.145	1.04
5	5.10	1147	4.87	0.0136	0.342	5.040	1.90	54	14.57	1410	5.39	0.0420	0.676	6.164	1.06
6	5.14	1128	4.85	0.0136	0.120	4.581	1.87	55	14.30	1410	5.39	0.0410	0.761	6.240	1.05
7	4.94	1212	5.06	0.0136	0.410	5.120	1.90	56	13.56	1350	5.22	0.0379	0.271	5.753	1.07
8	4.70	1234	5.13	0.0131	0.717	5.390	1.90	57	14.31	1350	5.22	0.0400	0.220	5.623	1.09
9	4.48	1266	5.22	0.0127	1.545	5.775	1.88	58	13.65	1320	5.19	0.0379	0.246	5.708	1.07
10	4.30	1292	5.28	0.0124	2.035	5.909	1.96	59	14.05	1245	4.99	0.0376	0.146	5.468	1.08
11	4.64	1197	5.02	0.0127	0.745	5.441	1.82	60	13.81	1320	5.19	0.0383	0.187	5.570	1.08
12	4.12	1344	5.42	0.0121	3.184	6.174	1.96	61	14.20	1320	5.19	0.0393	0.275	5.470	1.09
13	5.00	1287	5.40	0.0146	0.618	5.609	0.88	62	14.91	1440	5.45	0.0443	0.706	6.211	0.95
14	4.50	1287	5.40	0.0132	0.514	5.570	0.88	63	15.39	1470	5.51	0.0463	0.811	6.278	0.93
15	4.10	1363	5.46	0.0121	1.153	5.978	0.89	64	15.82	1440	5.45	0.0470	0.659	6.153	0.94
16	3.71	1390	5.53	0.0111	1.691	6.190	0.92	65	16.27	1410	5.39	0.0478	0.546	6.032	0.97
17	16.09	1184	5.00	0.0431	0.413	4.981	0.83	66	16.78	1351	5.26	0.0481	0.355	5.819	0.97
18	14.75	1185	4.99	0.0393	0.523	5.123	0.84	67	15.65	1470	5.51	0.0471	0.821	6.268	0.95
19	13.41	1335	5.39	0.0389	3.121	6.012	0.86	68	3.93	1465	5.68	0.0122	1.087	5.917	0.99
20	2.93	1605	5.76	0.0090	0.861	7.044	0.89	69	3.89	1308	5.32	0.0113	0.197	5.171	1.00
21	3.46	1440	5.45	0.0100	0.426	6.585	0.98	70	3.98	1308	5.32	0.0116	0.207	5.183	1.00
22	3.97	1410	5.39	0.0114	0.141	5.996	1.02	71	3.98	1400	5.54	0.0120	0.347	5.396	1.00
23	4.08	1410	5.39	0.0117	0.231	6.246	0.94	72	4.25	1300	5.30	0.0123	0.168	5.060	1.01
24	4.30	1350	5.25	0.0121	0.085	5.768	0.96	73	4.05	1313	5.34	0.0118	0.237	5.230	1.01
25	4.57	1320	5.19	0.0128	0.078	5.708	0.96	74	4.02	1420	5.59	0.0123	0.607	5.635	1.01
26	4.38	1380	5.32	0.0125	0.094	5.800	0.96	75	4.03	1335	5.39	0.0119	0.257	5.274	0.98
27	3.75	1470	5.52	0.0110	0.246	6.291	0.96	76	3.95	1405	5.55	0.0120	0.367	5.414	1.02
28	4.03	1470	5.51	0.0120	0.210	6.179	0.96	77	4.00	1363	5.45	0.0119	0.267	5.275	1.02
29	4.08	1470	5.51	0.0122	0.193	6.135	0.96	78	3.95	1450	5.65	0.0122	0.697	5.723	0.96
30	3.96	1502	5.58	0.0120	0.285	6.360	0.88	79	16.00	1405	5.55	0.0485	3.026	5.868	0.96
31	4.20	1455	5.48	0.0125	0.191	6.119	0.96	80	15.97	1395	5.53	0.0482	3.536	5.964	0.97
32	4.36	1410	5.39	0.0128	0.105	5.840	0.96	81	16.00	1230	5.11	0.0447	0.306	4.788	0.96
33	4.24	1440	5.45	0.0126	0.143	5.986	0.96	82	15.93	1230	5.11	0.0445	0.336	4.845	0.93
34	4.15	1440	5.45	0.0123	0.143	5.995	0.96	83	15.20	1210	5.06	0.0420	0.140	4.490	0.91
35	3.54	1502	5.58	0.0108	0.307	6.395	0.98	84	15.95	1244	5.15	0.0449	0.397	4.867	1.04
36	3.46	1605	5.77	0.0109	0.377	6.516	0.92	85	15.95	1220	5.09	0.0444	0.297	4.473	1.04
37	3.66	1527	5.63	0.0112	0.258	6.309	0.95	86	15.95	1320	5.35	0.0466	1.157	5.361	1.00
38	3.90	1356	5.33	0.0113	0.295	5.971	2.33	87	16.00	1255	5.19	0.0454	0.417	4.860	1.10
39	3.82	1304	5.21	0.0109	0.240	5.881	2.40	88	15.97	1255	5.19	0.0453	0.767	5.167	1.03
40	2.70	1580	5.80	0.0085	1.082	6.857	1.93	89	3.91	1435	5.53	0.0118	0.097	6.061	1.00
41	14.16	1440	5.45	0.0408	1.061	6.462	1.00	90	4.00	1405	5.45	0.0119	0.034	5.589	1.00
42	14.81	1410	5.39	0.0422	0.881	6.301	1.08	91	4.00	1435	5.53	0.0121	0.043	5.687	1.00
43	14.77	1395	5.35	0.0148	0.931	6.334	1.09	92	4.00	1450	5.55	0.0121	0.058	5.819	1.00
44	15.40	1395	5.35	0.0436	0.906	6.304	1.08	93	4.00	1450	5.55	0.0121	0.072	5.916	1.00
45	15.85	1380	5.35	0.0447	0.626	6.071	1.12	94	15.97	1318	5.26	0.0460	0.075	5.356	1.00
46	16.50	1350	5.25	0.0458	0.312	5.701	1.16	95	15.96	1265	5.12	0.0447	0.049	5.178	1.00
47	16.81	1380	5.32	0.0475	0.551	5.991	1.09	96	16.00	1235	5.05	0.0442	0.024	4.865	1.00
48	16.62	1380	5.32	0.0468	0.421	5.859	1.10	97	15.98	1250	5.09	0.0445	0.024	4.862	1.00
49	14.72	1423	5.41	0.0425	0.821	6.274	1.04	98	16.00	1235	5.05	0.0442	0.025	4.901	1.00

^a A = 1-16, B = 17-19, C = 20-40, D = 41-67, E = 68-78, F = 79-88, G = 89-93, H = 94-98. See Table I for initial oxygen: argon 20 ratios. $x \equiv 0.5 \times 10^3[\text{peak } ({}^{34}\text{O}_2)/\text{peak } ({}^{20}\text{Ar})]$.

D₂ mixture, using the observed relaxation times^{30a,b} the net time is given by the equation

$$\frac{1}{\tau_{av}} = \frac{X(\text{Ar})}{\tau_{\text{Ar-O}_2}} + \frac{X(\text{O}_2)}{\tau_{\text{O-O}_2}} + \frac{X(\text{D}_2)}{\tau_{\text{O}_2-\text{D}}} \quad (32)$$

We estimated that the presence of O₂-O₂ and O₂-D₂ collisions reduced the relaxation time only by about 20% over the O₂-Ar value. Another possibility is the effect of contaminant hydrocarbons. Lewis,³⁴ in a recent study of the HD exchange reaction, found that an HD sample slightly contaminated with unknown high molecular weight hydrocarbons had a noticeably higher self-exchange rate than the pure material. In the present study no attempt was made to look for the breakdown products of hydrocarbons, since these would be combusted by the excess oxygen and would

(34) D. Lewis, Cornell University, private communication.

have a smaller effect than the much higher D₂ impurity, which was shown not to be significant.

Closing Remarks

The bimolecular expression for atom switching, rate = $k[{}^{32}\text{O}_2][{}^{36}\text{O}_2]$, which adequately represents the data, permits two molecular mechanisms. The conventional one assumes collision between ³²O₂ and ³⁶O₂ molecules, each in Boltzmann equilibrium, with exchange taking place when the activation energy is in the translational mode. It does not follow the pattern established for other homogeneous exchange reactions (Table V). Also, the experimental activation energy is considerably lower than is anticipated for such a direct bimolecular process.

The observed rate relation can arise from a two-level vibrational excitation mechanism, assuming that the oxygen molecules are in Boltzmann equilibrium, but that exchange takes place only from a critical vibra-

tional level. However, this model is not consistent with the published oxygen-argon relaxation times. The "sum" rate expression, $\text{rate} = k([\text{}^{32}\text{O}_2] + [\text{}^{36}\text{O}_2])^2$, which also adequately represents the observed exchange rates, is a consequence of a two-level vibrational excitation model in which it is assumed that the rate of populating a critical vibrational level determines the rate of exchange. This model is consistent with the published oxygen-oxygen relaxation times but not with the oxygen-argon relaxation times.

The evidence for a vibrational excitation restriction in bimolecular exchange reactions is now impressive. Whereas shock tube data were instrumental in directing our attention to this mechanism, we have now independently demonstrated, on the one hand, that at room temperature vibrationally "hot" molecules produced by chemi-excitation readily exchange atoms,³⁵ and on the other, that when vibrationally cold molecules collide

with high relative kinetic energies (in center of mass coordinates, as in molecular beams) no exchange occurs.³⁶

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Appendix

Input data and bimolecular rates constants for set A-H are given in Table VIII.

(35) T. Baer, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1969.

(36) S. B. Jaffee and J. B. Anderson, *J. Chem. Phys.*, **49**, 2859 (1968)

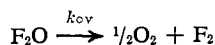
Reactions of Oxygen Fluoride in Shock Waves. I. Kinetics and Mechanism of Oxygen Fluoride Decomposition

M. C. Lin and S. H. Bauer

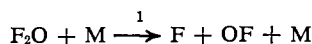
Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received July 1, 1969

Abstract: The thermal decomposition of F_2O was studied in a single-pulse shock tube over the temperature range 770–1390°K. For temperatures below 1000°K these results are in excellent agreement with the previous shock tube data; however, all rates obtained by conventional techniques, either in static or in flow systems, prove to be higher than those derived from the shock tube techniques. This is attributed to surface effects which cannot be avoided in conventional systems. Our present data are accounted for by the following scheme; $\text{F}_2\text{O} + \text{Ar} \rightleftharpoons \text{F} + \text{OF} + \text{Ar}$ (1, -1), $2\text{OF} \rightarrow 2\text{F} + \text{O}_2$ (2), $2\text{F} + \text{Ar} \rightleftharpoons \text{F}_2 + \text{Ar}$ (3, -3), with $k_1 = 10^{17.3 \pm 1.0} e^{-(42.5 \pm 4.1)/RT}$ cc/mole sec and $k_2 = 10^{12.10 \pm 0.12}$ cc/mole sec. The reverse reactions (-1) and (-3) cannot be neglected even in the early stages of reaction. The bond dissociation energy, $D(\text{FO-F})$, was found to be 42.7 ± 4.1 kcal/mole, on the basis of the RRKM theory. The mechanism of the F_2O_2 decomposition is also discussed.

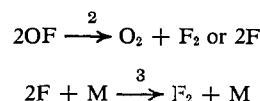
There are still uncertainties with regard to the kinetics and mechanism of the F_2O decomposition. The products of decomposition were found to be mainly F_2 and O_2 . The rates of the overall pressure changes are consistent with the following stoichiometry.¹



The activation energy for the overall process obtained by various methods, including the present study, is within the range 35 ± 5 kcal/mole.²⁻⁵ This value was believed to be associated with the rate-controlling step



Furthermore, it was postulated that the radical reactions which lead to the formation of F_2 and O_2



take place with little or no activation energy. The presence of F atoms and of OF radicals was demonstrated in the photochemical reactions of F_2O .^{6,7} It is thus reasonable to assume that the thermal decomposition of F_2O follows approximately the above scheme, including reactions 1-3.

All previous pyrolysis data were analyzed on the basis of this mechanism, with the assumption that reaction 2 was so fast that all reverse reactions were negligible, and accordingly that the observed overall rate constant, k_{ov} ,

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(2) L. Dauerman, G. Salsler, and Y. A. Tajima, *J. Phys. Chem.*, **71**, 3999 (1967); their *A* factor should be multiplied by 10.

(3) J. A. Blauer and W. C. Solomon, *ibid.*, **72**, 2307 (1968).

(4) W. C. Solomon, J. A. Blauer, and F. C. Jaye, *ibid.*, **72**, 2311 (1968).

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