

Isotopic Exchange Reactions of Atomic Oxygen produced by the Photolysis of NO₂ at 3660 Å*

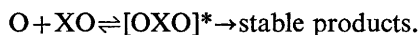
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Isotopically labelled atomic oxygen, produced by the photolysis of N¹⁸O₂ at 3660 Å, was allowed to react with CO, CO₂, N₂O, O₂ and COCl₂, respectively. The rates and mechanisms of the exchange reactions are discussed. The specific rate constants were determined for the process, O* + XO → O*X + O. They are $6.2 \times 10^{10} \exp [(-6900 \pm 700)/RT]$, $6.3 \times 10^8 \exp [(-3500 \pm 200)/RT]$, $9.6 \times 10^8 \exp [(-4400 \pm 800)/RT]$, and $3.9 \times 10^9 \exp [(-1100 \pm 400)/RT]$ l. mole⁻¹ sec⁻¹ for CO, CO₂, N₂O and O₂ respectively.

Atomic oxygen is produced in the ground state, O(³P), during the photodecomposition of NO₂ at 3660 Å. This means of obtaining oxygen atoms may be used to study reactions of atomic oxygen with simple molecules.¹ Two general types of reactions have been observed. In one case, the O(³P) adds to a molecule XO to yield stable products:



When a stable product is formed during the irradiation of a mixture of NO₂ and XO these two species compete for the oxygen atoms, and a change in the quantum yield for NO₂ dissociation results. This change may be employed to characterize the process as a function of the XO pressure. Examples of this behaviour have been reported for SO₂,¹ NO and NO₂.²⁻⁴

When no stable product is formed, the quantum yields remain unchanged relative to those for pure NO₂. However, the rates and mechanisms of the reactions may be determined by the measurement of isotopic oxygen exchange:

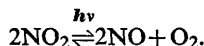


This type of reaction has been observed in the exchange with oxygen molecules.^{4, 5}

The purpose of this work was to study some reactions of the latter type. The method is applied to oxygen exchange reactions with CO, CO₂, O₂, N₂O and COCl₂.

EXPERIMENTAL

The general procedure was to add N¹⁸O₂ (~10 mm Hg) to the reaction cell by regular high-vacuum techniques. The NO₂ was irradiated at 3660 Å and constant temperature until a steady state of all species (O, NO, NO₂, etc.) was reached. The overall reactions were:



Thereupon, the gas of interest was introduced into the reaction cell, and irradiation at the steady state was continued for some time. The gas to be measured was then separated from the other components, and the ratio of isotopic oxygen abundances was determined. The experiments with molecular oxygen were carried out in a slightly different manner

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in order to avoid complicating exchange reactions. In this case, $^{18}\text{O}_2$ (98.2 atom % O^{18}) was mixed with N^{16}O_2 and irradiated at once for only a few minutes. Experiments were also performed to determine the extent of isotope exchange in the absence of photolysis. The results indicated that there was no appreciable exchange in the dark within the experimental error.

The reaction cell consisted of a quartz cylinder 10 cm long and 2 cm diam. The cell was wrapped with a smooth layer of aluminium foil to avoid gain or loss of light. A layer of insulated Nichrome wire was wound around the cell to permit heating. This was covered by a heavy layer of asbestos cord which provided adequate thermal insulation. The temperature of the cell was regulated by means of a Variac, and was determined by measuring the output of a calibrated iron-constantan thermocouple. The thermocouple was located in a well in the neck of the reaction cell just above the light path. The temperature variation during an experiment was less than $\pm 2^\circ\text{C}$.

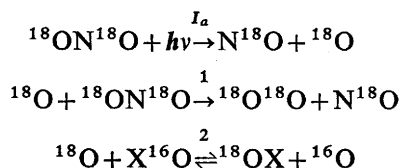
The samples were photolyzed with light from a medium pressure mercury lamp (G.E.H.-100-A4/T). The light was focused by means of a quartz lens. It was passed through selected filters ($\lambda = 3660 \text{ \AA}$, $\Delta\lambda = 50 \text{ \AA}$) and the reaction cell on to a solid-state photocell. The photocell was placed against the rear window of a second quartz cell (5 cm long) in tandem with the reaction cell. The second cell was evacuated, and served to insulate the photocell from the heated reaction cell. This precaution was necessary since the photocell output is sensitive to temperature changes. The output of the photocell was measured with a no. 7552 Leeds and Northrup potentiometer and simultaneously followed on a Mosely recording potentiometer. The absolute values of the incident and transmitted light were determined for each run by the photolysis of pure NO_2 under conditions of pressure and temperature which were identical with those of the sample mixture.

After photolysis, the samples were immediately separated from the NO_2 by fractional condensation. CO and O_2 were recovered by simply passing the reaction mixture through a liquid-air trap. Thus, NO_2 and NO (as N_2O_3) were effectively removed. Blank experiments, without irradiation, provided evidence that NO was not being collected in the sampling bulb. The ratio of mass 30 to mass 28 of CO was that of natural abundance, whereas, if NO of mass 30 had passed through, the ratio would have been high. CO_2 , N_2O and COCl_2 were first condensed in a liquid-air trap, the non-condensables were pumped off, and the trap was allowed to warm up to -80°C (dry ice+acetone). The NO_2 and N_2O_3 were retained in this trap, while the CO_2 , N_2O or COCl_2 was collected in the sampling bulb by means of a liquid-air trap. The isotopic oxygen ratios of the gases were measured with a Consolidated Engineering Corp. model 21-401 mass spectrometer. Preliminary experiments with COCl_2 showed that the changes in isotopic abundance of the COCl_2 were too small to be measured directly. Therefore, COCl_2 was dissociated over platinum wires at about 900°C , and the CO , thus produced, was recovered for mass-spectrometric analysis. Changes in isotopic abundances were determined by measuring the ratio, $\text{C}^{18}\text{O}/\text{C}^{16}\text{O}$.

The materials used in this study were c.p. and were further purified by appropriate trap-to-trap distillation. The isotopically enriched N^{18}O_2 was prepared by allowing $^{18}\text{O}_2$ (>98.2 atom % ^{18}O) to react with purified N^{16}O until the condensed product was show white. The resulting product contained 43.5 atom % ^{18}O . The ^{18}O was obtained by the electrolysis of D_2^{18}O . Before use, the oxygen was passed through liquid-air traps to remove condensables.

RESULTS

An expression for the experimental rate constants for CO , CO_2 , N_2O and COCl_2 may be derived from the simplified mechanism :



The rate of increase of ^{18}OX is given by

$$d(^{18}\text{OX})/dt = k_2([^{18}\text{O}][\text{X}^{16}\text{O}] - [^{16}\text{O}][^{18}\text{OX}]). \quad (1)$$

The measured change of the isotopic ratio, $R = [^{18}\text{OX}]/([^{18}\text{OX}] + [\text{X}^{16}\text{O}])$, is

$$\frac{\Delta R}{\Delta t} = \frac{d[^{18}\text{OX}]}{dt} \frac{1}{[\text{XO}]} = k_2[^{18}\text{O}]; \quad (2)$$

when $R \ll 1$ and the change in R is small. Assuming that steady state for $[^{18}\text{O}] = I_a/k_1[\text{NO}_2]$, and keeping $k_2[\text{XO}] \ll k_1[\text{NO}_2]$, one obtains

$$k_2 = (k_1[\text{NO}_2]\Delta R/\Delta t)/I_a. \quad (3)$$

Eqn. (3) was used to calculate the values of k_2 that appear in table 1. k_1 was taken 2 as $1.95 \times 10^{10} \exp(-1060/RT)$ l. mole $^{-1}$ sec $^{-1}$.

The exchange reactions with molecular oxygen were treated in an analogous manner except that the NO_2 used was of natural isotopic abundance, and $^{18}\text{O}_2$ was used for XO . The value of k_2 for oxygen was 5.8×10^8 l. mole $^{-1}$ sec $^{-1}$ at 298°K. This is similar to a mass spectrometric value of 6×10^8 l. mole $^{-1}$ sec $^{-1}$ obtained by Herron and Klein.⁴ However, no comparative values for the other constants are available. The logarithm of k_2 was plotted as a function of $1/T^\circ\text{K}^{-1}$ and a least-squares treatment of the data yielded the curves shown in fig. 1. Pre-exponential factors and activation energies were calculated and are also given in table 1.

TABLE 1.—RESULTS OF ISOTOPIC OXYGEN EXCHANGE REACTIONS
Rate constants, pre-exponential factors (log A) and energies of activation E

reactant	$T^\circ\text{K}$	k_2 , l. mole $^{-1}$ sec $^{-1}$	no. of expt. in average
CO	298	$(5.0 \pm 1.1) \times 10^5$	3
	364	$(4.2 \pm 0.7) \times 10^6$	2
	391	1.6×10^7	1
	$\log A = 10.8 \pm 0.4$ * $E = 6.9 \pm 0.7$ kcal/mole		
CO ₂	298	$(1.8 \pm 0.03) \times 10^6$	4
	310	2.6×10^6	1
	358	$(4.1 \pm 0.03) \times 10^6$	3
	395	6.6×10^6	1
	$\log A = 8.8 \pm 0.8$ $E = 3.5 \pm 0.2$ kcal/mole		
O ₂	298	$(5.8 \pm 1.2) \times 10^8$	5
	335	$(7.4 \pm 2.7) \times 10^8$	3
	352	$(9.1 \pm 1.0) \times 10^8$	2
	362	9.5×10^8	1
	381	$(8.0 \pm 1.1) \times 10^8$	4
	402	$(1.0 \pm 0.2) \times 10^9$	3
	$\log A = 9.6 \pm 0.5$ $E = 1.1 \pm 0.4$ kcal/mole		
N ₂ O	298	$(5.5 \pm 0.1) \times 10^5$	2
	332	8.5×10^5	1
	343	1.8×10^6	1
	358	$(2.0 \pm 0.6) \times 10^6$	2
	$\log A = 9.0 \pm 0.9$ $E = 4.4 \pm 0.8$ kcal/mole		
COCl ₂	298	$(1.9 \pm 0.4) \times 10^6$	2

* A is given in l. mole $^{-1}$ sec $^{-1}$.

The results of the experiments with COCl_2 are reported at room temperature only. At higher temperatures, the results were scattered. The scatter in the data may be due to wall reactions such as those described by Noyes⁶ for the $\text{Cl} + \text{COCl}_2$ reaction. However, the trend in the rate constant as a function of temperature was similar to that for CO_2 . Therefore, it is estimated that the activation energy for the $\text{O} + \text{COCl}_2$ reaction is about 3 kcal/mole.

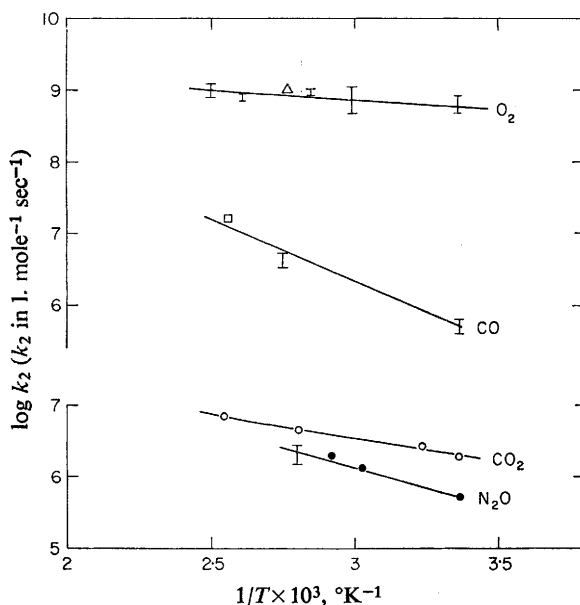
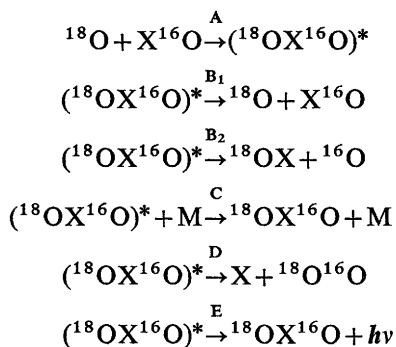


FIG. 1.—Log k_2 as a function of $1/T$.

Two experiments were conducted with normal NO_2 and H_2^{18}O . However, rapid exchange between NO_2 and H_2O molecules occurred in the dark. Therefore, the exchange of $^{16}\text{O} + \text{H}_2^{18}\text{O}$ cannot be studied by the present method.

DISCUSSION

One may assume that the mechanism of production of $\text{O}(^3P)$ atoms by the photolysis of NO_2 is well established at 3660 \AA .⁷⁻¹⁰ As a result, the oxygen exchange reactions may be discussed in terms of the simple scheme: 1, 2



In the general case, this mechanism predicts the formation of an excited intermediate (OXO)*. The intermediate may vary in stability from a transition state to a relatively stable complex. An example of a "stable" intermediate is NO_3^* ,¹¹ which is similar to that obtained in the reaction, $\text{O} + \text{NO}_2$. The knock-off mechanism suggested by Yamazaki and Cvetanovic¹² would be represented by the case in which the (OXO)* complex behaves like a transition state.

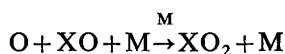
By assuming steady-state conditions for $[\text{}^{18}\text{OX}^{16}\text{O}]^*$ and that $[\text{X}^{18}\text{O}]/[\text{X}^{16}\text{O}] \ll 1$, one obtains for the rate of exchange:

$$\frac{d[\text{X}^{18}\text{O}]}{dt} = \frac{k_A k_{B_2} [\text{}^{18}\text{O}][\text{X}^{16}\text{O}]}{k_{B_1} + k_{B_2} + k_C[\text{M}] + k_D + k_E} \quad (4)$$

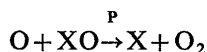
One may neglect a small isotope effect and write $nk_{B_1} = k_{B_2}$, in which n is the number of equivalent oxygen atoms in XO. Combining eqn. (4) with eqn. (2), one obtains

$$k_A = ((n+1)k_{B_1} + k_C[\text{M}] + k_D + k_E)k_2/nk_{B_1} \quad (5)$$

If one compares the rate expressions for each of the following overall reactions:



and



with the rate expression for the detailed mechanism, then

$$k_M(\text{M}) = (k_C[\text{M}] + k_E)k_2/nk_{B_1} \quad (6)$$

and

$$k_p = k_D k_2/nk_{B_1} \quad (7)$$

Eqn. (6) and (7) may be substituted in (5), yielding

$$k_A = k_2(n+1)/n + k_M[\text{M}] + k_p \quad (8)$$

Since the specific rate constants k_2 , k_M and k_p (all experimentally determinable) are known for the systems studied, k_A may be evaluated. Using the values of k_2 , k_M and k_p summarized in table 2, k_A was calculated at 25°C. The values of k_A are also given in table 2.

Mahan and Solo¹⁹ have measured the rate of formation of an intermediate, CO_2^+ , which resembles reaction A in this study. Their specific rate constant at room

TABLE 2.—RATE CONSTANTS k_A AT 25°C, RELATIVE RATES, AND DATA USED IN THE CALCULATION OF k_A

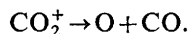
reactant	k_A l. mole ⁻¹ sec ⁻¹	$\frac{k_A}{nk_{A\text{CO}}}$	k_2 l. mole ⁻¹ sec ⁻¹	k_M l.2 mole ⁻² sec ⁻¹	k_p l. mole ⁻¹ sec ⁻¹	ref.		
						k_2	k_M	k_p
CO	1.0×10^6	1	5×10^5	1×10^7 to 1.4×10^5	—	c	14	—
N ₂ O	1.1×10^6	1.1	5.5×10^5	none ^a	1.0×10^{-9} ^b	c	—	15, 16
CO ₂	2.7×10^6	1.4	1.8×10^6	none	—	c	—	—
COCl ₂	3.8×10^6	3.8	1.9×10^6	none	—	c	—	—
O ₂	0.9×10^9	450	5.8×10^8	3.6×10^8	—	c	3, 13	—
SO ₂	1.1×10^9	550	6.7×10^8	1.4×10^{10}	—	1	1	—
NO	2.0×10^9	2000	1.1×10^9	3.73×10^{10}	10^{-12}	4	2	17
NO ₂	9.6×10^9	4800	4.2×10^9	1.0×10^{11}	3.28×10^9	4	18	2

(a) "None" is used to indicate the cases in which no stable XO_2 is formed.

(b) The rates of both reactions, $\text{O} + \text{N}_2\text{O} \rightarrow 2\text{NO}$ and $\text{O} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$ are of the same magnitude.

(c) this work.

temperature was 1×10^4 l. mole⁻¹ sec⁻¹. This is two orders of magnitude smaller than our k_A for CO. The difference may be attributed to, in part, the unusual [M] dependence they found, or to their neglect of the reverse reaction,



This reaction is important in our exchange measurements.

The value of $1.1\text{--}2.05 \times 10^5$ l. mole⁻¹ sec⁻¹ found by Avramenko and Kolesnikova²⁰ is less than an order of magnitude smaller than our k_A for CO. However, in both cases, the activation energies do not agree with that found for the present exchange reaction. It is possible that, since all three experimental methods are different, the rate constants do not represent exactly comparative processes.

Although a number of experiments have been reported^{12, 20-22} on the reactions of excited oxygen atoms, O(¹D) and O(¹S), with CO, CO₂ and N₂O, no specific rate constants were derived. Therefore, no comparison of the exchange reactions of excited oxygen atoms with the present results is possible at this time.

Pre-exponential factors A were calculated for the Arrhenius equation which represents k_A . This was done by assuming that the activation energies for reaction A are equal to those for reaction 2. Comparison of these pre-exponential factors with the calculated collision frequencies led to the value of the steric factors which are presented in table 3. These values are only worthy of qualitative comparison

TABLE 3.—CALCULATED STERIC FACTORS

reactant	Z_{AB} , calc.*, l. mole ⁻¹ sec ⁻¹	$P = A/Z_{AB}$, calc.
CO	8.9×10^{10}	~ 1
CO ₂	1.1×10^{11}	8.6×10^{-3}
N ₂ O	1.1×10^{11}	1.7×10^{-2}
O ₂	8.2×10^{10}	7.2×10^{-2}

* $Z_{AB} = 2.74 \times 10^{25} \sigma_{AB}^2 (T/\mu)^{\frac{1}{2}}$ l. mole⁻¹ sec⁻¹; $\sigma_{AB} = (\sigma_A + \sigma_B)/2$. The collision diameters were taken from Moelwyn Hughes, *Physical Chemistry*, 2nd ed. (Pergamon Press, Oxford, 1961).

since the pre-exponential factors are subject to rather large errors. The estimated collision frequencies are dependent on the choice of the collision diameter σ_{AB} . CO₂ and N₂O show similar steric factors which are consistent with their similar linear structures. The results imply that attack of O atoms on the C atom in CO₂ and the central N atom in N₂O occurs with nearly equal probabilities. However, the value of P for the O+CO reaction indicates the absence of steric hindrance.

According to the mechanism presented here, the rate of formation of the intermediate (OXO)* is proportional to the rate of isotopic oxygen exchange. One should, therefore, consider some of the factors that influence the formation of (OXO)*, and attempt to correlate these factors with our knowledge of the properties of the reactant molecules. The factors include a favourable steric configuration, available bonding orbitals, and a reasonably low, spin-allowed, energy state for (OXO)*.

The reactants given in table 2 seem to fall into at least three groups on the basis of their relative rates of reaction A. Group I, with relatively low k_A includes CO, N₂O, CO₂ and COCl₂. For N₂O, CO₂ and COCl₂, there would be a moderately high amount of steric hindrance which would impair the attack of O atoms on the central atom of the molecule. In addition, none of these molecules has a readily available bonding orbital. Evidence that these molecules do not form stable intermediates is deduced from the fact that no stable XO₂ products are formed. The formation of stable molecules requires sufficient lifetime of the intermediate so that

it can be deactivated by binary collisions with M. The possibility of deactivation by fluorescence would not change the general conclusions.

CO, in group I, seems to be an exception. CO exhibits little steric hindrance, has a bonding orbital available, and can form stable CO₂. The slow rate of formation of stable CO₂ by reaction of O(³P) with CO has been attributed^{19, 20, 23, 24} to the spin forbidden process of deactivation of the triplet state of CO₂ to a singlet ground state. It is probable that the formation of the intermediate (OCO)* reflects this difficulty requiring a relatively high activation energy. The stability of (OXO)* for group I should, therefore, approach that of a transition state.

Group II, consisting of SO₂ and O₂, shows relatively high rates for reaction A. Since both O₂ and SO₂ offer little steric hindrance and have available bonding orbitals, it is expected that they form intermediates (OXO)* with relatively high stability. There is a low energy state for (O₃)* as evidenced by the low activation energy (1.1 kcal mole⁻¹) for exchange. Further evidence for the stability of (O₃)* is the rate of formation of O₃.²⁵ It may be assumed that the stability of (SO₃)* is even greater than that of (O₃)* by comparing the relative rates of reaction M.^{1, 4}

Group III, consisting of NO and NO₂, exhibits the fastest rates of formation of (OXO)*. This results from the lack of steric hindrance and the active free radical configurations of the molecules which allow them to form bonds readily. Broida, Schiff and Sugden²⁶ have assigned a long lifetime for (NO₂)* while Guillory and Johnston¹¹ have confirmed the stability of the OONO intermediate.

The results of the present study show that isotopic exchange reactions may be able to supply us with information concerning the nature and stability of the excited intermediates. More additional rate data are necessary to complete the quantitative evaluation of the results of this study. When more data are available concerning either of the reactions C, D or E for the reactants employed here, values for the specific rate constants for individual steps of the proposed mechanism may be evaluated.

¹ Jaffe and Klein, *Trans. Faraday Soc.*, 1966, **62**, 2150.

² Klein and Herron, *J. Chem. Physics*, 1964, **41**, 1285.

³ Kaufman, in *Progr. Reaction Kinetics*, vol. 1, ed. Porter (Pergamon Press, Oxford, 1961).

⁴ Herron and Klein, *J. Chem. Physics*, 1964, **40**, 2731.

⁵ Brennen and Niki, *J. Chem. Physics*, 1965, **42**, 3725.

⁶ Noyes, *J. Amer. Chem. Soc.*, 1951, **73**, 3039. Noyes and Fowler, *J. Amer. Chem. Soc.*, 1951, **73**, 3043.

⁷ Ford, *Can. J. Chem.*, 1960, **38**, 1780.

⁸ Blacet, Hall and Leighton, *J. Amer. Chem. Soc.*, 1962, **84**, 4011.

⁹ Ford and Jaffe, *J. Chem. Physics*, 1963, **38**, 293.

¹⁰ Pitts, Jr., Sharp and Chan, *J. Chem. Physics*, 1964, **40**, 3655.

¹¹ Guillory and Johnston, *J. Chem. Physics*, 1965, **42**, 2457.

¹² Yamazaki and Cvetanovic, *J. Chem. Physics*, 1964, **40**, 582.

¹³ Benson, *J. Chem. Physics*, 1963, **38**, 1251.

¹⁴ Leighton, *Photochemistry of Air Pollution* (Academic Press, New York, 1961).

¹⁵ Fenimore and Jones, *8th Combustion Symp.*, 1961, p. 127.

¹⁶ Kaufman, Gerri and Bowman, *J. Chem. Physics*, 1956, **25**, 106.

¹⁷ Kaufman and Decker, *7th Combustion Symp.* (Butterworths, London, 1959), p. 57.

¹⁸ Ford and Endow, *J. Chem. Physics*, 1957, **27**, 1156.

¹⁹ Mahan and Solo, *J. Chem. Physics*, 1962, **37**, 2669.

²⁰ Avramenko and Kolesnikova, *Bull. Acad. Sci. U.S.S.R.*, 1959, 1506.

²¹ Katakis and Taube, *J. Chem. Physics*, 1962, **36**, 416.

²² Werneck, *J. Chem. Physics*, 1964, **41**, 3435.

²³ Kondratiev and Ptichlin, *Kinetika in Kataliz*, 1961, **2**, 492.

²⁴ Raper and Demore, *J. Chem. Physics*, 1964, **40**, 1053.

²⁵ Benson and Axworthy, *J. Chem. Physics*, 1957, **26**, 1718.

²⁶ Broida, Schiff and Sugden, *Trans. Faraday Soc.*, 1961, **57**, 259.