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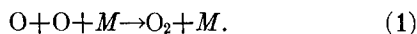
Recombination of Oxygen Atoms in the Absence of O₂*

J. E. MORGAN,† L. ELIAS, AND H. I. SCHIFF

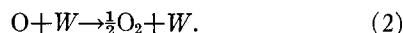
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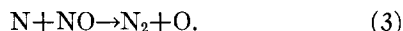
THE gas phase recombination of oxygen atoms in systems containing more than 90% O₂ occurs largely through the intermediate formation of ozone.^{1–3} It is therefore difficult in such systems to study the direct atom recombination



Although several authors have measured the rate constant for this reaction in the presence of O₂,^{4–6} it seemed desirable to determine this quantity in an O₂-free system. Under these conditions, atom recombination can occur only by reaction (1) and on the wall



Oxygen atoms were generated by the reaction



The nitrogen atoms were produced by subjecting N₂ to a microwave discharge. NO was added through an inlet to the gas stream in a manner described previously.¹ Excess of either reactant results in chemiluminescence—yellow with excess NO, blue with excess N atoms. An intermediate "dark" condition can then be obtained, which corresponds to equimolar amounts of both reactants. Under these conditions the gas stream contains only O atoms and N₂. Furthermore the concentration of O atoms formed can be accurately deduced from the flow rate of NO required to titrate the N atoms.

The O atom concentration was measured as a function of distance (or time) from the NO inlet by two methods. In the first method an excess of NO₂ was

added through a second inlet which could be moved axially along the reaction tube. The products were trapped downstream and the amount of NO produced was taken as a measure of the O-atom concentration at the movable inlet position. The atom concentrations determined in this manner along the reaction tube extrapolated to the value of the NO concentration required to titrate the N atoms at the stationary inlet. This is significant, since it shows the mutual consistency of the determination of O atoms by NO₂ titration with the production of O atoms by reaction (3).

In the second method, a fixed flow of NO was introduced through the movable inlet and the resulting chemiluminescence measured photometrically. The relative intensities at this inlet, as it was moved along the tube, were taken as a measure of the relative atom concentrations at those positions. These measurements gave results identical to those obtained by the first method.

The integrated rate expression for reactions (1) and (2) is

$$k_2 t = \ln \frac{[\text{O}]_0}{[\text{O}]} - \ln \left(\frac{k_2 + k_1[\text{O}]_0[M]}{k_2 + k_1[\text{O}][M]} \right),$$

where [O]₀ is the initial atom concentration. For very low pressures ([M] → 0), the atom concentration should follow a pseudo first-order behavior, an observation which can be used to calculate k₂ in the following manner. Plots of ln[O] vs time yielded curves which were approximately linear for the experimental conditions used. The average slopes of these curves of course depend on [M]. However, when these slopes are plotted as a function of [M], they must extrapolate to a true value of k₂ at zero pressure. For this apparatus k₂ was found to be 0.40 sec^{−1}, which corresponds to a recombination coefficient γ = 1.6₅ × 10^{−5}. Once the value of k₂ is obtained, the integrated rate equation can be rearranged to permit an evaluation of k₁ for each experiment. The results of the work to date are summarized in Table I; the average value of k₁ = 3.2₃ × 10¹⁵ mole^{−2} cm⁶ sec^{−1}.

The measurement of [O] by isothermal calorimetry has been used previously in this laboratory¹ to study discharged O₂. When used in the present system, this technique gave much higher atom concentrations, as well as a faster recombination rate, than did the methods outlined above. The presence of some additional

TABLE I.

Pressure (mm)	10 ⁹ [O] ₀ (mole cm ^{−3})	10 ⁹ [O] (mole cm ^{−3})	t (msec)	10 ^{−15} k ₁ (mole ^{−2} cm ⁶ sec ^{−1})
2.30	1.18 ₅	0.97 ₅	218	3.6 ₄
2.50	1.03 ₅	0.87 ₂	198	3.7 ₆
3.15	1.44 ₈	1.18 ₀	242	2.7 ₈
3.90	1.45 ₀	1.16 ₅	153	3.8 ₈
4.55	1.73 ₀	1.36 ₅	148	3.0 ₉
4.80	1.42 ₅	1.01 ₀	278	2.6 ₈

species which liberates heat to the calorimeter seems to be a reasonable explanation for this discrepancy. The heat liberated by O atoms was calculated from the results of the NO₂ titration method and subtracted from the total measured heat. This showed that the second species decayed by first-order kinetics, which suggests a collisional deactivation process. The half-life of 50 msec for this species agrees with Kaufman's estimate for vibrationally excited N₂.⁷

Further work is in progress for studying this species as well as for determining the temperature coefficient for O-atom recombination.

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† Holder of National Research Council of Canada Studentship.

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The $^1\Sigma^+$ Excited States of Carbon Monoxide*

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IF the ultraviolet spectra of diatomic molecules made up of atoms of the first row are calculated using the LCAO-MO-SCF orbitals calculated for the ground state using 1s, 2s, and 2p atomic basis functions, some of the lower excited states seem to be well represented by single electron excitations from occupied to virtual orbitals. The states which lie near the ionization potential are, on the contrary, poorly represented by single excitations and are often predicted to lie far higher than the ionization energy.¹⁻³ Configuration interaction in this limited basis does not appear to improve matters for these high-lying states.

Although we are using computer programs for the present calculations which make it possible to undertake more complicated work than has been customary, it still is a matter of great importance to find the simplest calculation that will give useful results. Any unnecessary increase in the number of basis orbitals in these

calculations greatly increases the over-all computer time required. For this reason it has seemed worthwhile to evaluate the effect of two different and, to a certain extent, complementary modifications to the set of atomic basis orbitals: (1) use of several *L*-shell orbitals with different exponents; (2) use of *M*-shell orbitals.

To test these effects we have recently recalculated the vertical excitation energies of the $B^1\Sigma^+$, $C^1\Sigma^+$, and $E^1\Sigma^+$ states of CO. Experimentally these are found

TABLE I. Exponents of orbitals in double *L*-shell calculation.

For C: 1s, 5.673, 2s, 2.4, 2s', 1.2, 2pσ, 2.4, 2pσ', 1.2, 2pπ, 2.4, 2pπ', 1.2
For O: 1s, 7.658, 2s, 3.37, 2s', 1.685, 2pσ, 3.37, 2pσ', 1.685, 2pπ, 3.37, 2pπ', 1.685

about 11 eV above the ground state with equilibrium internuclear distances approximately the same as that of the ground state.

Herzberg and Hugo⁴ have attributed these states to $\pi \rightarrow \pi$ and $\sigma \rightarrow \sigma$ single electron excitations, respectively. The LCAO-MO-SCF orbitals calculated with the usual 1s, 2s, and 2p atomic functions gave predicted energies more than twice too high.^{1,2}

We have calculated the SCF orbitals for CO with two exponents for each of the functions in the *L* shell. These exponents are given in Table I. The lowest

TABLE II. $^1\Sigma^+$ states of CO.

State	Exp. Vert. excitation energy (ev) ^a	3s-3p Calculation (ev) after first-order CI	Double <i>L</i> shell (ev) after first order CI	Single <i>L</i> shell (ev)
$X^1\Sigma^+$	0	0	Excitation	0
$B^1\Sigma^+$	10.78	11.12 mostly $\sigma \rightarrow \sigma$	18.01 $\sigma \rightarrow \sigma$	23.14 $\pi \rightarrow \pi$
$C^1\Sigma^+$	11.40	11.78 mostly $\sigma \rightarrow \sigma$	23.99 $\pi \rightarrow \pi$	27.37 $\sigma \rightarrow \sigma$
$E^1\Sigma^+$	11.52	13.32 mostly $\sigma \rightarrow \sigma$		

^a Y. Tanaka, A. S. Jursa, and F. Le Blanc, *J. Chem. Phys.* **26**, 862 (1957).

$\sigma \rightarrow \sigma$ excitation is at about 21 eV and the lowest $\pi \rightarrow \pi$ excitation is also at about 2 eV. Here, as in the earlier calculation,¹ configuration interaction does not make a marked difference.

Using a basis-set made up of 1s, 2s, 2p, 3s, and 3p atomic functions with exponents given by Slater's rules, it is found that the energies of the virtual orbitals are markedly lowered as compared with those found in the double exponent calculation and are rather close together. Since this is a case of near degeneracy, configuration interaction is important here, although a very small effect in the other calculations. From a six-term CI function (containing both $\sigma \rightarrow \sigma$ and $\pi \rightarrow \pi$ excitations), it is found that the two lowest states both correspond largely to $\sigma \rightarrow \sigma$ excitations and the calculated