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OZONE PHOTOLYSIS: A DETERMINATION OF THE
ELECTRONIC AND VIBRATIONAL STATE DISTRIBUTIONS
OF PRIMARY PRODUCTS

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The energy distributions of the primary products of photolysis reactions are of twofold significance. First, the distributions are determined by, and thus are a probe of, the detailed dynamics of unimolecular dissociation. The final product state distribution can lend information on the nature of the potential energy surfaces involved. Secondly, the information on the energy disposal of photolysis products is needed in order to understand secondary reactions that these photolysis products may undergo. Such secondary reactions of dissociation products of ozone are of particular interest at present for atmospheric chemistry as they are of importance in modeling the competing depletion and creation processes of the stratospheric ozone layer.¹

When UV radiation is absorbed by ozone in the Hartley band ($220 \text{ nm} < \lambda < 300 \text{ nm}$), the photodissociation products have been measured in the past to be exclusively $\text{O}(^1\text{D}) + \text{O}_2(^1\Delta_g)$.² Wavelength dependence of the quantum yield for $\text{O}(^1\text{D})$ product has been

measured^{3,4} and found to be constant over the range from 250-300 nm. Thus, it has been assumed that only $O(^1D)$ and $O_2(^1\Delta_g)$ are produced over the entire wavelength range. The reasoning, however, is indirect. Recently, two experiments^{5,6} have been performed which used more direct methods. The results, however, were not in agreement.

First, Fairchild et al.⁵ have applied molecular beam photofragment spectroscopy to this problem for several wavelengths between 275 and 300 nm. They reported that approximately 10% of the total products were produced in the ground electronic state [$O(^3P) + O_2(X^3\Sigma_g^-)$]. In this experiment, a chemi-ionization detector was employed, followed by a quadrupole mass spectrometer, for the detection of oxygen atom produced. The product energy distribution, which provides information for state identification, was measured by time-of-flight analysis. The relative yield of ground state products was found to be fairly constant over the wavelength range investigated.

Amimoto et al.⁶ have measured the time dependence of the concentration of $O(^3P)$ after photolysis of ozone with a pulsed KrF laser at 248 nm. The results of their studies indicate no production of $O(^3P) + O(X^3\Sigma_g^-)$ within their experimental error.

We wish to report here the high resolution molecular beam measurement of the translational energy distribution of the primary photolysis products of ozone at 266 nm. We have determined the relative populations of the internal degrees of freedom from the features which appear in the product translational energy

distribution and the consideration of the conservation of total energy. The resolution was sufficient to separate both the electronic and vibrational states of the photolysis products. If one takes the bond energy of ozone to be 23.9 kcal/mole⁷ and uses standard values for the energies of the states of O⁸ and O₂,⁹ then the energetically accessible and spin allowed channels are:

The excess energy of process (1) is sufficient to populate vibrational levels up to $v = 21$. For process (2) the maximum excitation is $v = 3$. Only the ground vibrational state would be energetically allowed for process (3). Experiments were carried out by crossing a supersonic molecular beam of ozone seeded in argon at a right angle with the frequency quadrupled output of a pulsed Nd:YAG laser. The measurements were performed in our new high resolution universal crossed molecular beam apparatus. The time-of-flight spectrum of the O₂ fragments was obtained from an electron bombardment mass spectrometer which is rotatable in the plane of the beams and has a flight path of 34 cm. The laser was operated at 10 pulses per second with 35 millijoules per pulse quadrupled output.

With this technique it has been possible to clearly resolve products corresponding to processes (1) and (2) and also to clearly resolve all four of the vibrational levels of process (2). Products from process (3), even if they are produced, have insufficient translational energy to enter our detector, which was placed off axis from the molecular beam. Figure 1 shows the time of flight spectrum of the O_2 fragment taken with the detector 30 degrees off axis from the ozone beam. The signal was accumulated for 150,000 laser shots with an unfocused beam. Five peaks were observed which correspond to most probable center-of-mass translational energies of ~60, 13.4, 10.4, 6.4 and 2.4 kcal/mole. The only channel which can give product energies greater than 15.8 kcal/mole is the production of $O(^3P) + O_2(^3\Sigma_g^-)$. Thus we assign the entirety of the fastest peak to this process. The remaining four peaks correspond well to the energies expected for the $v = 0, 1, 2$ and 3 levels of $O_2(^1\Delta_g)$ from process (2).

Figure 2 shows the transformation of data shown in Fig. 1 to the center-of-mass energy space. The data was smoothed with a five channel polynomial filter¹⁰ and time-dependent background was removed before transformation.¹¹ It is clearly seen that a substantial amount of $O_2(^3\Sigma_g^-) + O(^3P)$ was produced. The integrated area of this channel is approximately 10% of the total products. If the ionization efficiencies of $O_2(^3\Sigma_g^-)$ and $O_2(^1\Delta_g)$ yielding O_2^+ are approximately equal, our results are in agreement with the findings of Fairchild et al.⁵ Carrying out a more thorough analysis of the $O_2(^1\Delta_g) + O(^1D)$ product manifold using additional polarization dependence data, we have obtained relative yields of the vibrational states of 57% $v = 0$;

24% $v = 1$; 12% $v = 2$; and 7% $v = 3$. The exact position of the peak of $O_2(^1\Delta, v = 0)$ indicates that approximately 17% of the remaining energy is deposited in rotational excitation. This is what one would calculate assuming an impulsive energy release from a geometry near that of the ground state of ozone.

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† IBM Postdoctoral Fellow, 1977-78.

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FIGURE CAPTIONS

Fig. 1. Photofragment time-of-flight spectrum for O_2 fragments produced by photodissociation of O_3 at 266 nm.

Fig. 2. Data of Fig. 1 converted into center-of-mass energy space. Data was smoothed and time-dependent background was subtracted before conversion.

Fig. 1

FLIGHT TIME (MICROSECONDS)

Fig. 2.

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