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Dolphus E. Milligan and Marilyn E. Jacox

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Infrared Spectroscopic Evidence for the Species HO_2 [†]

DOLPHUS E. MILLIGAN[‡] AND MARILYN E. JACOX Mellon Institute, Pittsburgh 13, Pennsylvania (Received 8 February 1963)

Infrared absorptions observed following the photolysis of mixtures of HI and O₂ in an Ar matrix at 4°K appear to be contributed by HO₂ produced in the matrix. Studies on isotopically substituted systems support this assignment. The two oxygen atoms have been shown to be nonequivalent. Approximate force constants and thermodynamic functions for HO₂ are tabulated.

INTRODUCTION

THE study of the kinetics of various chemical reac-L tions has for many years required the postulation of the species HO₂ as an important intermediate. However, most attempts to detect this species directly have ended in failure. Recently, the detection of HO₂ using the techniques of mass spectrometry has been achieved, and very recently Foner and Hudson¹ have succeeded in producing observable amounts of this free radical by some six different reactions and have given more accurate values for the ionization potential of HO_2 and for the dissociation energy, $D(H-O_2)$. These workers also present an excellent review of earlier attempts to confirm the existence of HO_2 and to determine its properties.

Several initially promising attempts to observe the infrared spectrum of HO₂ have ended in later disappointment. Giguère² observed an infrared absorption at 1305 $\rm cm^{-1}$ in the frozen products of an electrical discharge through water vapor. This band was initially assigned to HO₂ but was later found to be contributed by N₂O₃ produced because of nitrogen impurity in the sample.³ Cashion and Polanyi,⁴ studying chemiluminescence from the system $H+O_2$, found evidence for an infrared emission which could plausibly arise from HO₂. Later experiments by Charters and Polanyi,⁵ using a different apparatus, failed to confirm these observations.

The reaction of H atoms produced by the photolysis of HI in a CO matrix at 20°K has been shown by Ewing, Thompson, and Pimentel⁶ to yield sufficient amounts of the radical HCO for infrared studies. Their identification of this species has been confirmed by the electron spin resonance studies of Adrian, Cochran, and Bowers⁷ on a similar system. Using an argon matrix containing 9% HCN and 1% HI, Cochran, Adrian, and Bowers⁸ have also measured an appreciable electron spin resonance signal assigned to H₂C=N following photolysis. Hence, it appeared promising to study the photolysis of HI (or HBr) in the presence of small amounts of O_2 trapped in an argon matrix. The present paper presents the results of an nfrared study on this system.

EXPERIMENTAL DETAILS

The oxygen (Matheson Company, extra-dry grade) was stated to have 99.6% minimum purity and was used without further attempts at purification. In some experiments, oxygen enriched to 27.7% O18 or to 96.3% O¹⁸ (Iosmet Corporation) was used.

HBr (Matheson Company) used in these experiments had a stated minimum purity of 99.8%, and HI (Matheson Company) of 98.0%. DBr was produced by the reaction of D₃PO₄ with anhydrous NaBr, and DI by the reaction of D_3PO_4 with anhydrous KI. These gases were further purified by drying in a column of P_2O_5 and by repeated condensation at 77°K to remove noncondensable material. Appreciable deuterium-hydrogen exchange at the walls of the vacuum system prevents an accurate estimate of the deuterium content of the resulting materials.

Argon (Air Reduction Company) was used without further purification.

Samples were prepared by standard manometric procedures. It was important to prepare the DI and the gas mixtures in a darkened room and to store them in bulbs heavily wrapped in dark cloth. To prevent premature photolytic decomposition, sample depositions were made through a vacuum system wrapped in aluminum foil. A fresh sample was prepared for each experiment. In earlier experiments, separate mixtures of hydrogen (deuterium) halide in argon

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[‡] Present address: National Bureau of Standards, Washington

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^{36, 1938 (1962).}



FIG. 1. Ar:O₂(27.7%O¹⁸):HI=200:4:1. Spectrum following photolysis. Present in initial sample.

and oxygen in argon were simultaneously deposited on the cold window. However, it was later found that this precaution was unnecessary, provided that the small amounts of hydrogen halide and oxygen were not condensed together in the sample bulb.

The cell used for these observations has been described previously.⁹ Sample depositions onto a CsBr window were carried out at temperatures approaching 4°K, using liquid helium as coolant. After initial studies had established that the absorptions of interest were indeed produced by photolysis of the sample, it was possible to produce higher yields of the new species by simultaneous deposition and photolysis of the cold film, avoiding the filtering effect of the halogen produced upon photolysis.

Sample irradiations were carried out using a General Electric AH-4 medium-pressure mercury arc. The sample irradiation window used for these experiments was of KBr, with an estimated cutoff near 2200 Å.

All spectra were recorded on a Beckman IR-7 spectrometer, estimated to have a resolution and frequency accuracy of $\pm 1 \text{ cm}^{-1}$ in the range 650-4000 cm⁻¹ under the conditions of the experiments here reported.

OBSERVATIONS

In a typical experiment the Ar:HX ratio ranged between 50 and 200 and the O_2 :HX ratio between 1 and 4. Relatively high concentrations of Ar and of O_2 were found to give the most satisfactory yield of photolysis product. The role of the Ar matrix is judged to be an essential one. Photolysis of HI, which occurs very readily in a sample of gaseous HI exposed to room light, is considerably less efficient in the matrix. Apparently, most of the H atoms are trapped in the "cage" in which they are produced. There they are rapidly deactivated by collisions with surrounding atoms, and recombination with the nearby I atoms occurs. However, some diffusion of H atoms in the Ar lattice appears to be possible, and these atoms are free to combine with other reactive species, such as oxygen. In the photolysis of HI suspended in solid O_2 , it would be predicted that an H atom would readily react with O_2 adjacent to the "cage" containing the I atom. This HO₂ radical would then be free to react with the I atom. Hence, it seems less likely that significant yields of HO₂ might be obtained by photolyzing HI in an O₂ matrix.

Typical experiments involved the deposition of between 100 and 200 mm Hg of sample, drawn from a 2-liter bulb at a rate of approximately 2 mm per min. Photolysis periods of from about 30 to 60 min were used. Particularly in experiments on deuterated samples, there was some difficulty with severe sample deterioration during the first few minutes of photolysis. This was marked by an orange coloration of the film, which often peeled from the cold window. Although no conclusive data on this phenomenon have been gathered, it seemed to occur more often when the sample had been rapidly deposited and showed visible cracks. Apparently, it results from poor thermal contact between the low-temperature window and the sample.

Experiments were performed on Ar:O₂:HBr, Ar:O₂: HI, Ar: O¹⁸₂: HI, Ar: O₂(27.7% O¹⁸): HI, Ar: O₂: DBr, Ar:O₂:DI, and Ar:O¹⁸₂:DI mixtures. The absorptions appearing after photolysis showed no dependence on the nature of the halogen, although HI and DI photolyses generally gave a somewhat higher yield than did HBr and DBr photolyses. In a few experiments in which the photolysis was conducted through a BaF₂ window (approximate cutoff 1900 Å) only traces of the most intense product absorption appeared. This suggests that the photolysis product is itself decomposed by radiation between about 2200 Å, the cutoff of KBr, and 1900 Å. Such a secondary photolysis of a radical species has previously been reported by Adrian, Vochran, and Bowers⁷ for HCO produced by the photolysis of formaldehyde. Infrared studies in our laboratory have indicated that the primary product in the reaction of H atoms with HCN, presumably H₂CN, also undergoes further photolysis.

Table I summarizes the various absorption frequencies observed for the photolysis products of the present experiments, and Fig. 1 shows the resulting absorptions in the $\operatorname{Ar:O_2(27.7\% O^{18}):HI}$ experiment. Before photolysis, there were no background absorptions in the regions shown in Fig. 1 except that at 1399 cm⁻¹, which remained unchanged during photolysis. Presumably it is contributed by HDO remaining in the deposition line from a previous experiment, since it is not present in most other experiments and appears only when appreciable H₂O or D₂O absorptions are also present. Comparison with the spectrum of an $\operatorname{Ar:H_2O_2}$ sample indicates that no H₂O₂ is produced upon photolysis.

The absorptions reported in Table I are stable upon warmup of the sample to 35°K. However, they dis-

⁹ D. E. Milligan, J. Chem. Phys. 35, 1491 (1961).

Ar:O2 ¹⁶ :HI	Ar:O2 ¹⁸ :HI	Ar:O ₂ (27.7% O ¹⁸):HI	Ar:O ₂ ¹⁶ :DI	Ar:O ₂ ¹⁸ :DI	
 1101	1040	1040	1020	982 (w)	
		1069.5		998	
		1072			
		1101			
1389.4	1380.3	1380.3			
		1383.6			
		1386.0			
		1389.4			
3414	3402	3402	2530	2499	
		3414		2515	

TABLE I. Photolysis product frequencies (cm⁻¹) observed in Ar:O₂:HI experiments employing isotopic substitution.

appear between this temperature and 42°K, near which point diffusion is known to occur in the argon matrix.

DISCUSSION

The above results indicate that a species stable only at very low temperatures has been produced in the argon matrix. Since no shift has been observed in the absorptions produced using HBr (or DBr) rather than HI (or DI), the species appears not to contain halogen. The presence of hydrogen is, of course, indicated by the gross changes in the spectrum upon deuteration. The paucity of the absorptions observed in the deuterated samples is an inconclusive indication that the species contains only one H atom. The slight shift in frequency when O¹⁸₂ is substituted for ordinary O_2 is a positive indication of the presence of oxygen in the species. Furthermore, the more complex absorption pattern observed in the 27.7% O18 experiment, in which approximately 40% of the molecular oxygen is present as O¹⁶O¹⁸, furnishes positive evidence for the presence of two nonequivalent O atoms in the species. Hence, there appears to be little doubt that the infrared spectra of HO₂ and its isotopic modifications have been observed.

Theoretical predictions of the molecular geometry of HO₂ concur in indicating that the ground state of this species should be bent, but their estimate of the HOO angle covers a wide range. Walsh¹⁰ has concluded that HO₂ should be slightly more bent than HNO, from which it differs by the addition of an electron to the a''- π -orbital, whose contribution to the binding energy is approximately independent of the angle of the molecule. Dalby¹¹ has determined that the HNO angle in the ground $({}^{1}A')$ state of this species is 108.5° and that the HNO angle in the first excited state $({}^{1}A'')$

increases to 116.2°. Hence, Walsh's theory predicts that the ground $({}^{2}A'')$ state of the species HO₂ should have an HOO angle near 108°. Furthermore, Walsh predicts that the radical should have at least one allowed low-lying electronic transition, ${}^{2}A' - {}^{2}A''$, polarized perpendicular to the molecular plane, with an increased HOO angle in the upper $({}^{2}A')$ state.

More recent predictions of the HOO angle seem to indicate the possibility of an approach to the symmetry of an isosceles triangle. The application of Linnett's theory of electron distribution to HO2¹² would favor an angle between 55° and 70°. Theoretical calculations recently carried out by Boyd¹³ have the rather surprising result that HO₂ should have an isosceles triangle configuration in its ground state, with an HOO angle of 47° for the assumed bond distances.

Because present work has demonstrated that the two O atoms are nonequivalent and because Walsh's theory has achieved considerable success in predicting other molecular configurations, it appears reasonable to use angles of 90° and 120° for estimates of force constants and thermodynamic properties. It has also been necessary to assume distances for the O-H and O-O bonds. Boyd, considering the bond distances of related

TABLE II. Force constants derived from frequencies observed for HO¹⁶₂ in an argon matrix.

	<h00=90°< th=""><th><hoo=120°< th=""></hoo=120°<></th></h00=90°<>	<hoo=120°< th=""></hoo=120°<>
F _{OH} (dyn/cm)	6.46×10 ⁵	6.46×10^{5}
$F_{\rm OO}({\rm dyn/cm})$	6.23×10 ⁵	6.11×10 ⁵
$F_{\rm HOO}({\rm dyn}\cdot{\rm cm})$	0.87×10 ⁻¹¹	0.84×10 ⁻¹¹

¹² M. Green and J. W. Linnett, J. Chem. Soc. **1960**, 4959.
¹³ M. E. Boyd, J. Chem. Phys. **37**, 1317 (1962).

 ¹⁰ A. D. Walsh, J. Chem. Soc. **1953**, 2288–2293.
¹¹ F. W. Dalby, Can. J. Phys. **36**, 1336 (1958).

TABLE	III.	Thermody	ynamic	properties	of	HO_2	(cal/mole.°K)
	for	$R_{\rm OH} = 0.95$	8 Å, <i>R</i> c	$h_{00} = 1.30 \text{ Å},$, <	HOO	=120°.

T (°K)	C_p^0	$(H^0 - H_0^0)/T$	$-(F^0-H_0^0)/T$	<i>S</i> °
273.16	8.23	8.00	44.26	52.26
298.16	8.34	8.02	44.96	52.98
300	8.35	8.02	45.00	53.02
400	8.91	8.17	47.33	55.50
500	9.49	8.38	49.17	57.55
600	9.99	8.61	50.72	59.33
700	10.41	8.84	52.07	60.91
800	10.77	9.06	53.26	62.32
900	11.10	9.27	54.34	63.61
1000	11.37	9.47	55.33	64.80
1100	11.62	9.65	56.24	65.89
1200	11.84	9.83	57.09	66.92
1300	12.03	9.99	57.88	67.87
1400	12.21	10.16	58.62	68.76
1500	12.35	10.28	59.32	69.60
2000	12.90	10.88	62.37	73.25
3000	13.40	11.65	66.94	78.59

species, has chosen 0.958 and 1.30 Å as the respective bond distances. These values have also been adopted for the present studies.

Force constants have been determined by direct expansion of the secular determinant for HO^{16}_{2} , separating out the high frequency by the usual approximation.¹⁴ Two sets of force constants were obtained for the bending and O \div O stretching modes. One of these sets could, however, be excluded because of its poor fit in the corresponding relationships for $HO^{16}O^{18}$. The resulting values are given in Table II.

The value for $F_{\rm OH}$ is independent of the angle of the molecule. Using the appropriate mass parameters and this value, the O–H stretching vibrations of HO¹⁸O¹⁶ and HO¹⁸₂ can easily be predicted to appear at 3402 cm⁻¹. The appearance of an absorption at that frequency in the O¹⁸-substituted systems is gratifying.

It is interesting and helpful to note that, if the 1101 cm^{-1} absorption in HO¹⁶² is taken to be the O \div O stretching absorption, and if the mass of the H atom is added to that of its neighboring O atom, the simple

"diatomic molecule" approximation predicts absorptions in the 1040–1100 cm⁻¹ region within 0.5 cm⁻¹ of the values reported in Table I. Furthermore, it indicates that the 1072 cm⁻¹ absorption should be assigned to HO¹⁸O¹⁶, and the 1069.5 cm⁻¹ absorption to HO¹⁶O¹⁸. This observation was used in eliminating one of the sets of calculated force constants, as previously mentioned.

Unfortunately, application of these relationships to an expanded set of data including $\rm HO^{16}O^{18}$ frequencies does not permit an accurate estimate of the HOO angle, since its cosine is proportional to the difference between two large quantities. Nevertheless, the present estimates of force constants and thermodynamic properties for HO₂ appear to be meaningful, as they are relatively insensitive to the molecular angle.

The values found for the frequencies and force constants appear reasonable for the species HO₂. The O-O stretching frequency of H₂O₂ is 880 cm⁻¹, while the stretching frequency of O₂ is 1580 cm⁻¹. A value of 1101 cm⁻¹, then, seems reasonable for a species of intermediate bond type. Wilson (reference 14, p. 175) estimates O-O stretching force constants to lie in the range $3.5-5.0 \times 10^5$ dyn/cm. The force constant for O₂ is 11.8×10^5 dyn/cm. Hence, the presently observed value of about 6×10^5 dyn/cm seems appropriate for an O-O bond. The force constants and frequencies assigned to the OH bending and stretching modes agree quite well with values found for ordinary molecules.

The lower frequency data for DO¹⁶₂ and DO¹⁸₂ appear to be somewhat anomalous. Even in experiments in which the 1020 (or 998) cm^{-1} absorption is at least as intense as that at 1390 cm⁻¹ in HO¹⁶₂, no welldefined second absorption appears, although there is a very broad, weak absorption near 1075 cm⁻¹, and DO¹⁸₂ has a sharp, weak absorption at 982 cm⁻¹. Whether either of these absorptions should be attributed to the missing fundamental is open to some question. Product rule estimates including the observed lower frequency place the missing frequency at 1083 cm⁻¹ for DO¹⁶₂ and at 1049 cm⁻¹ for DO¹⁸₂, choosing the molecular angle as 120°. These estimates are quite insensitive to the angle. For the unlikely possibility of a linear molecule, in which the two lower frequency modes are of different symmetry types and are separately calculable, DO162 should have its lower frequency absorptions at 1066 and 1069 cm⁻¹. Anharmonicity should tend to increase somewhat all of these predicted frequencies. Possibly the occurrence of Fermi resonance leads to complications in the spectra of the deuterated species.

The approximate thermodynamic functions of HO₂ are given in Table III, assuming that the HOO angle is 120°. These values, like those for the force constants, are relatively insensitive to the molecular angle; if the HOO angle is reduced to 90°, the values of C_p° and $(H^{\circ}-H_0^{\circ})/T$ remain unchanged, while the values for

¹⁴ E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), pp. 74–76.

 $-(F^{\circ}-H_{0}^{\circ})/T$ and S° are each increased by only 0.24 cal/mole ·°K.

CONCLUSIONS

The infrared spectra of HO2 and of its various deuterium- and oxygen-18-substituted counterparts have been observed following photolysis of oxygenhydrogen halide mixtures in an argon matrix held near 4°K. The two oxygen atoms are certainly nonequivalent, but an accurate estimate of the molecular angle appears not to be feasible from present data. Force constants and thermodynamic properties have been tabulated for this species, assuming appropriate molecular dimensions.

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Use of Catalytic Probes to Determine Atom Concentrations and Atom Diffusion Coefficients*

J. E. MORGAN AND H. I. SCHIFF

Upper Atmosphere Chemistry Group, McGill University, Montreal, Canada

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A simple analysis is presented for the perturbation of a stream of partially dissociated gas by a catalytic probe capable of completely removing all the atoms from the stream. The results of this analysis were confirmed by experiments on discharged O2, which showed that for linear flow rates of several meters per second the atom concentration reaches 99% of the unperturbed value within 2.5 cm upstream from the probe. It is shown that such a probe can be used to measure atom concentrations, since the flux to the probe remains finite even though the atom concentration at its surface is virtually zero. No appreciable errors are introduced into relative concentration measurements required to obtain first order rate constants. Under suitable experimental conditions, absolute concentrations can be obtained which are negligibly different from the unperturbed values regardless of the order of the recombination processes. A method is described for using such a probe to obtain accurate values of atomic diffusion coefficients which does not require accurate knowledge of heterogeneous or homogeneous recombination rates.

THE perturbation of the atom concentration in a partially dissociated gas stream caused by the introduction of a catalytic probe has been discussed by Wise and Ablow.¹ They concluded that this perturbation would have introduced an error of 10³ in the firstorder rate constant calculated by Elias et al.² from probe measurements of oxygen atom recombination in partially dissociated O_2 . In the present paper a simple analysis is presented to show that an error of this magnitude could not have been caused in this way. Experimental evidence is presented as a test of this analysis, which also shows that probe measurements can be used to provide accurate diffusion coefficient data.

Let us consider first an unperturbed gas flowing with a linear velocity v through a tube of cross-sectional area a. The concentration of atoms must be low enough that their removal does not appreciably affect the total molar flow rate. Radial diffusion can be neglected, since its effect can be made negligible for suitably chosen experimental conditions.

The steady-state conditions lead to the equation

$$D(d^{2}c/dx^{2}) - v(dc/dx) - kc = 0, \qquad (1)$$

where D is the diffusion coefficient, c is the concentration at some position x along the tube, and k is the first-order rate constant for oxygen atom recombination by the mechanism

$$O + O_2 + O_2 \rightarrow O_3 + O_2, \tag{I}$$

 $0 + 0_3 + 20_2$ (II)

$$O + wall \rightarrow \frac{1}{2}O_2.$$
 (III)

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¹ H. Wise and C. M. Ablow, J. Chem. Phys. **35**, 10 (1961). ² L. Elias, E. A. Ogryzlo, and H. I. Schiff, Can. J. Chem. **37**, 1680 (1960).