THE INFRARED ABSORPTION SPECTRUM OF HYDROXYL RADICALS IN SOLID ARGON

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Received 18 May 1988; in final form 8 July 1988

By means of the reaction of atomic H or D (produced either in a microwave discharge or on a W filament) with either NO_3 or O_3 or atomic O, we have prepared and trapped OH and OD radicals in solid Ar at 12 K, characterized by their infrared absorption lines at 354820 and 261610 m⁻¹, respectively. The reasons for these spectral assignments, and for the rejection of the previously published assignments, are discussed.

1. Introduction

The neutral hydroxyl radical OH, an important intermediate species in many atmospheric and combustion reactions, has been well characterized in the gaseous phase by its rotational [1], vibration-rotational [2] and rovibronic [3] transitions in the infrared, visible and near ultraviolet regions of the electromagnetic spectrum. Although the measurement [4] of the vibronic photoluminescence of the hydroxyl radical in solid neon has enabled the determination of both some electronic and vibrational spectral parameters pertinent to this environment, for this radical in solid argon, which is a host matrix much more commonly used than neon, conflicting assignments [5,6] of the wavenumbers of the fundamental vibrations of OH and OD that were proposed many years ago remain unresolved.

The objective of the present experiments has been to make possible a definitive assignment of this characteristic spectral feature so as to permit analytical applications of this information. Toward this objective, our experiments have been conducted differently from the previous ones in several ways. First, we have employed advanced spectrometric instrumentation with much improved sensitivity and wavenumber accuracy. Second, instead of photolytic methods, we have used known chemical reactions as three different sources of OH radicals. Third, we have produced atomic hydrogen from H_2 not only by means of a microwave discharge but also by thermal dissociation on a tungsten filament. Fourth, we have employed isotopically labeled reactants, specifically D and ¹⁸O, as well as a full range of control experiments. In this paper, we focus attention upon the most interesting and urgent aspect of the results of these many experiments, namely the definitive assignment of infrared spectral lines to hydroxyl radicals in solid argon; other aspects will be discussed in a separate publication.

Both our great range of variation of conditions of preparation and stabilization of the radicals and the conditions of measurement of the spectrum permit an unambiguous assignment not only to some OH species but also to the neutral OH radical in particular. The experiments and their significance are described in the following sections.

2. Experiments

The absorption spectra of samples deposited onto a CsBr crystal in an Air Products Displex refrigerator were recorded by means of a Bomem DA3.002 interferometric spectrometer with a CaF₂ beam splitter and a Hg/Cd/Te detector cooled with liquid N₂. Spectra were measured at a resolution of 50 m⁻¹ in the range 120000-400000 m⁻¹. Under these conditions the wavenumber accuracy and reproducibility are both 5 m⁻¹, or larger as limited by the width of spectral lines, but our reported wavenumbers are rounded to the nearest 10 m⁻¹. To produce the solid

0 009-2614/88/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) deposits we used two inlet systems, similar to those depicted as A and B in fig. 1 of a previous report [7]. One system consisted of two separate gas streams that intersected just before the deposition surface; each stream could be subjected to microwave discharge. In this system, one discharge tube could be replaced with a different tube containing a W filament surrounded by a water-cooled jacket. The second system consisted of a single inlet tube to the cryostat with a mixing region upstream into which two separate streams of gas could be led; one microwave cavity was used with this system. Mounted opposite the inlet port, a window of fused silica allowed the illumination of the sample by a medium-pressure Hg lamp (Gates MLA100).

Three reactions have been used to prepare the samples for spectrometric examination. With the double inlet system, separate streams of H_2 in Ar and O_2 in Ar were each excited by means of microwaves at 2.45 GHz with absorbed power typically 10-20 W. In other experiments only the stream of H_2 in Ar was excited, and the other stream of reactant was either NO_2 or O_3 in an Ar carrier. Because the reaction [8] of atomic H with O_3 is less rapid than that [9] with NO_2 (at least in the gaseous phase), the single inlet system permitted an improved extent of reaction in this case. Other experiments involved the reaction of NO2 or discharged O2 with D2 instead of H_2 with the double inlet system; furthermore, discharged ¹⁸O₂ or mixtures of ¹⁶O₂ and ¹⁸O₂ were reacted with discharged H_2 and/or D_2 in the same system. With the W filament reactor replacing the second discharge unit, H₂ or D₂ in Ar in one stream passing the hot filament was reacted with NO₂ in Ar in the other stream.

The nominal purities of the bottled gases were Ar 99.9995%, ${}^{16}O_2$ 99.97%, H₂ 99.999%, ${}^{18}O_2$ 99.5% and D₂ 99.5%. The mixtures of H₂ and Ar were passed through a trap at 77 K to remove possible contaminants before entering the microwave discharge. NO₂ was prepared by the slow reaction of NO (nominally 99% pure) with excess O₂, and was stored under O₂ at a pressure $\approx 2 \times 10^5$ Pa for at least 24 h before use. O₃ was prepared by means of an electrodeless discharge of O₂ and stored in a trap, containing silica gel, that was kept below 195 K; during the experiments, Ar gas passed the trap to carry the O₃ into the flow system. An ozone meter that utilized the ab-

sorption by O₃ of light at 254 nm was used to determine the concentration of ozone, varying within the range 0.001-0.005 molar fraction in Ar. The other mixtures of reactants were prepared according to standard techniques. The molar fractions in Ar were varied within the ranges 0.0005-0.01 for H₂ or D₂ or their mixtures in the discharge experiments but 0.025-0.1 for H₂ (but constant 0.0033 for D₂) in the pyrolysis experiments, 0.002-0.01 for ¹⁶O₂ or ¹⁸O₂ or their mixtures, while the molar fraction of NO₂ in Ar was 0.001. In different experiments with the W filament, the power supplied to the filament was varied, thus varying the temperature; no measurement of the filament temperature was carried out, but the orange colour in the most successful experiments indicated ≈ 1600 K. Flows of gaseous mixtures were measured with Tylan mass flow meters; flow rates in each stream of gas were in the range 1.4-4.0 µmol s⁻¹. The periods of deposition on CsBr at ≈ 12 K of the reaction products were 30-90 min.

For purposes of comparison, the absorption spectra of H_2O , D_2O , a mixture of H_2O_2 and H_2O , and of HNO_3 , all at varied molar fractions in Ar, were also measured. Dissolved gases were removed from the deionized H_2O , D_2O or HNO_3 before sampling to form the gaseous mixture with Ar. Gases were also removed from the liquid mixture of H_2O_2 and H_2O in an unknown ratio before preparation of a gaseous sample at a total molar fraction of 0.002 in Ar. Other control experiments with the double inlet system included $H_2 + NO_2$, $H_2 + O_3$, and $H_2 + O_2$ without discharge, O_2 + discharged H_2 , and H_2 + discharged ${}^{18}O_2$.

3. Results

Absorption spectra of mixtures deposited without microwave discharge showed the characteristic lines, if any, of the reactant species plus adventitious H_2O and minute traces of CO and CO₂. When one or both discharges were operated, additional lines appeared in the spectra, shown in figs. 1 and 2. The essential results are that narrow lines appeared at 354820 m⁻¹ when discharged H_2 was reacted with NO₂, O₃ or discharged ¹⁶O₂, at 353710 m⁻¹ when discharged H_2 was reacted with discharged H_2 was reacted with discharged H_2 , and at both these wavenumbers when discharged H_2 was reacted with a discharged mixture of ¹⁶O₂ and ¹⁸O₂, similarly in



Fig. 1. Infrared absorption spectra of products in Ar matrices at 12 K from the reactions of (A) discharged H_2 (0.003)+discharged $^{18}O_2$ (0.003); (B) discharged H_2 (0.003)+ discharged mixture of $^{16}O_2$ (0.002) and $^{18}O_2$ (0.003); (C) discharged H_2 (0.003)+discharged $^{16}O_2$ (0.003); (D) NO₂ (0.001)+discharged H_2 (0.005), and (E) O₃ (0.001)+discharged H_2 (0.003). The numbers in parentheses indicate molar fractions in Ar in each stream.

experiments with discharged D₂, narrow lines appeared at 261610 m⁻¹ when discharged D_2 was reacted with NO₂ or discharged ¹⁶O₂, and at 260030 m⁻¹ when discharged D₂ was reacted with discharged ${}^{18}O_2$. When a discharged mixture of H₂ and D_2 was reacted with discharged ¹⁸ O_2 , narrow lines appeared at 353710 and 260030 m⁻¹. Beside these lines, lines due to the appropriate isotopic variants of H₂O [10], H₂O₂ [11], HO₂ [7], HNO [7,12] and HONO [13] have been assigned on the basis of their spectra from either published data or our own measurements. The line at 354820 or 261610 m^{-1} appeared in experiments when pyrolyzed H_2 or D_2 was reacted with NO₂. Previously attributed to OH radicals in solid Ar [6], lines at 345230 and 342800 m^{-1} were observed in some experiments when discharged H_2 was reacted with NO₂ or O₃ or discharged O₂, and



Fig. 2. Infrared absorption spectra of products in Ar matrices at 12 K from the reactions of (A) discharged D_2 (0.003)+discharged $^{18}O_2$ (0.003); (B) discharged D_2 (0.002)+discharged $^{16}O_2$ (0.002), and (C) NO₂ (0.002)+discharged D_2 (0.005). The numbers in parentheses indicate molar fractions in Ar.

at 254330 and 252620 m⁻¹ [6] in some experiments of discharged D_2 reacted with NO₂ or discharged O_2 . In the experiments with H_2 at the smallest molar fractions in the discharged stream reacted with NO₂, the line at 354820 m⁻¹ and those attributed to HO₂, HONO and HNO were recorded at a large ratio of signal to noise, but both lines at 345230 and 342800 m^{-1} were either very weak or entirely absent; the relative intensities of the latter lines in our experiments are inconsistent with previous results [6]. In experiments in which the temperature of the sample was transitorily increased to ≈ 25 K, the intensities of the lines at 354820 or 261610 m⁻¹ decreased (irreversibly) to a much greater extent than nearby lines due to known stable species, whereas the intensity of the line at 345230 m⁻¹ increased during the same thermal operation.

In some experiments involving illumination of the samples by a Hg lamp after deposition, the lines assigned to HO_2 or DO_2 were practically eliminated. The intensities of the lines at 354820 or 261610 m⁻¹ decreased only slightly. Initially absent after depo-

sition in an experiment with discharged H_2 and NO_2 , a line at 342790 m⁻¹ appeared after photolysis, whereas the weak line at 345230 m⁻¹ became more intense; another line at 354960 m⁻¹, present in the H_2O blank spectrum and assigned to H_2O aggregate, became more intense after photolysis, and two new lines at 351890 and 352230 m⁻¹, assigned to HNO₃, appeared at the same time.

4. Discussion

Postponing consideration whether this species carries a net electrical charge, we first assign the four lines at 354820, 353710, 261610 and 260030 m⁻¹ to the isotopic variants ¹⁶OH, ¹⁸OH, ¹⁶OD and ¹⁸OD respectively. The reasons for these assignments are the following. Because of the behaviour on warming the matrix, the carrier is a reactive species, but because of the stability to ultraviolet light it is not easily photolyzed, unlike HO₂ radicals. Because these lines appear when reactants containing only H and O are used, the carrier contains only these elements. Because in the presence of both H and D but only ¹⁶O, only two lines with the appropriate intensity characteristics appear, the carrier contains one and only one hydrogen atom. Because in the presence of both ¹⁶O and ¹⁸O but only H, only two lines with the appropriate intensity characteristics appear, the carrier contains one and only one oxygen atom. The sharpness of the lines makes the latter test very sensitive. For instance, in the case of HO₂, also formed in these experiments, the significantly greater line width at 341280 m⁻¹ in the presence of both ¹⁶O and ¹⁸O seems to indicate that both H¹⁶O¹⁶O and $H^{16}O^{18}O$ absorb at that wavenumber, although two lines are distinguished at 340180 and 339980 m⁻¹ for H¹⁸O¹⁶O and H¹⁸O¹⁸O respectively (based on the appearance of the latter line in experiments with only ¹⁸O); approximate calculations [14] confirm very small isotopic shifts of wavenumber for the HO₂ species in these circumstances. Finally the appearance of the specified four lines under our experimental conditions having the smallest molar fractions of reactants is entirely consistent with the carrier containing only one H and one O.

Furthermore we assign these four lines to the neutral hydroxyl radical OH (and its isotopic variants), thus to neither the OH⁺ cation nor the OH⁻ anion. The reasons for this assignment are the following. In the gaseous phase the centre of the vibration-rotational band [15] of ¹⁶OH⁺ is at 295937.24 m⁻¹, hence far from our line at 354820 m⁻¹. We have used three chemical reactions well known to produce OH radicals in experiments in the gaseous phase:

(a) Mixtures of H_2 and O_2 gases with Ar were separately discharged in the double inlet system; then reacted together [16]:

$$H+O \longrightarrow OH;$$

(b) a discharged mixture of H_2 and Ar gases reacted with a mixture of NO_2 and Ar gases in the double inlet system [9]:

$$H + NO_2 \rightarrow OH + NO;$$

(c) a discharged mixture of H_2 and Ar gases reacted with a mixture of O_3 and Ar gases in the single inlet system [17]:

$H + O_3 \rightarrow OH + O_2$.

In the gaseous phase M represents any molecule that serves catalytically as a third body to promote stable union. In our experiments with the double inlet system, the residence periods and the partial pressures in the gaseous region in which the streams of reactants mix before deposition are so small that the efficiency of homogeneous combination is small; instead the surface of the depositing matrix itself acts as the 'third body" [7]. However, the fact that the efficiency of OH production was much greater for the reaction $H+O_3$ in the single inlet system than in the double inlet system proves both that in the former case the homogeneous combination was significant and that the radicals formed in the gaseous phase were trapped efficiently so as to enable their detection. Microwave discharges of mixtures of H₂ and Ar are known to form [18], beside H atoms, metastable atoms, ions and free electrons; although reactions of such ions and electrons with NO₂ might conceivably produce OH⁺ or OH⁻, the pyrolysis of H₂ on a W filament at moderate temperatures produces cleanly H atoms [19] and no such ions. Thus confirming the other evidence, the production of the lines at 354820 or 261610 m⁻¹ in the experiments with NO₂ and pyrolysis of H_2 or D_2 , respectively,

demonstrates conclusively that the carriers are electrically neutral.

Furthermore the following facts support these assignments:

(a) These lines were not observed in control experiments (in which H_2 or D_2 were not discharged), and no alternative assignments of these lines are known to us; although the 354820 m⁻¹ line appeared very weakly in an experiment with O_2 reacted with discharged H_2 , the possible sequence of rapid reactions [20]

$$H + O_2 \xrightarrow{M} HO_2$$
,

 $H + HO_2 \rightarrow 2 OH$

can explain this appearance, whereas the reaction of H_2 with discharged O_2 produced no such line.

(b) These lines were observed at the smallest molar fractions of reactants used in our experiments and at their greatest intensities relative to those of HO_2 and H_2O under those conditions, indicating that these absorptions are not due to complexes or aggregates of OH involving other than Ar atoms.

(c) Whenever these lines appeared, they were always sharp, the linewidth (53-56) m⁻¹) being essentially that of the nominal resolution at which the spectrometer was operated – again this small linewidth is strong evidence for a successfully isolated species.

(d) The measured wavenumbers assigned to ¹⁶OH and ¹⁶OD are close to those of the centres, 356963.788 and 263206.01 m⁻¹, of the corresponding fundamental vibration-rotational bands [2] of the ¹⁶OH and ¹⁶OD radicals, respectively, in the gaseous phase, and those small displacements are in fact well within the common range of such matrix shifts [21]; although the line assigned to ¹⁶OH trapped in Ar is even closer to the band centre 355560.57 m⁻¹ of the fundamental vibration-rotational band [22] of the ¹⁶OH⁻ ion, we have already demonstrated that our lines belong to OH radicals, not anions.

(e) The ratio 1.35629 of the wavenumbers of the matrix lines assigned to ¹⁶OH and ¹⁶OD is similar to that (1.35621) of the band centres of the corresponding gaseous radicals [2], and also to that (1.35688) deduced from the experiments with Ne matrices [4].

(f) The displacement 1110 m^{-1} of wavenumber

from ¹⁶OH to ¹⁸OH in the matrix samples is similar to that (1115 m⁻¹) from ¹⁶OH⁻ to ¹⁸OH⁻ in the gaseous phase [22] (pertinent data for ¹⁸OH in the gaseous phase are unavailable), but different from the displacements 617 m⁻¹ for ν_1 and 1436 m⁻¹ for ν_3 from H₂¹⁶O [23] to H₂¹⁸O [24]; such a displacement is consistent with the carrier being a diatomic species containing only O and H; the displacements 1110 m⁻¹ from ¹⁶OH to ¹⁸OH and 1580 m⁻¹ from ¹⁶OD to ¹⁸OD agree well with the values (1120 and 1589 m⁻¹ respectively) calculated from data for OH and OD in the gaseous phase.

(g) In the same experiments in which production of OH or OD radicals was attempted, the lines of H_2O or D_2O were much more intense than in control experiments; these species are expected products of the further reaction of OH or OD radicals with H or D atoms. Moreover, because in control experiments without discharge of D_2 or ¹⁸O₂ there were no discernible lines due to D_2O , $H_2^{18}O$ or $D_2^{18}O$, all these products could have resulted from the reaction of H or D atoms with the ¹⁶OD, ¹⁸OH and ¹⁸OD radicals. As well as lines due to NO₂, HNO, HONO, NO and other species, the line at 354820 m⁻¹ has also been observed in experiments involving the photodecomposition of HNO₃ in solid argon. These experiments will be described in detail in a separate paper.

We next consider the previous assignments of infrared absorption lines to the OH and OD radicals. The present control experiments, and much other evidence published since 1964, indicate that the line [5] at 357300 and 263400 m⁻¹ are due to H_2O and D_2O molecular species, respectively, in some state of aggregation with species other than Ar atoms, despite their near coincidence with the wavenumbers 357400 and 263500 m⁻¹ of the fundamental vibrations of OH and OD subsequently inferred from the photoluminescence of these radicals trapped in solid Ne [4]. The other sets of lines, 345230 and 342820 m⁻¹ for ¹⁶OH and 254320 and 252620 m⁻¹ for ¹⁶OD, attributed previously [6] to these radicals have also been observed in some of the present experiments, and the line at 344170 m^{-1} (but none at 353710 m^{-1}) appeared weakly in the blank experiment in which undischarged H₂ was reacted with discharged $^{18}O_2$; however, the relative intensity and the shapes of the lines in these doublets are variable, and these lines become practically undetectable in the experi-

ments with the smallest molar fractions of reactants. The width of each line appears significantly greater than the spectral slit widths in the reported measurements [6], and the matrix shifts from the band centres of the radicals in the gaseous phase are much larger than expected [21]. Both these facts and the very existence of doublets have never been satisfactorily explained. These effects strongly indicate that these spectral lines may be attributed to OH or OD mojeties of complexes or aggregates rather than to the diatomic molecular radicals surrounded by Ar atoms. On the other hand, careful examination of the published spectrum [6] reveals a possible line near 354800 m⁻¹ that may indicate the previous unwitting detection of the OH radical; unfortunately a plot of the corresponding region for the OD radical was not published. Similarly a line near 354500 m^{-1} was reported to be produced after photolysis of HNNN in the presence of O_2 in an N_2 matrix [25].

Two spectral lines at ≈ 355400 and 354890 m⁻¹, not separated under the conditions of poor resolution [26], have been recently assigned to the ¹⁶OH⁻⁻ species. Whereas the latter, more intense line almost coincides with that at 354820 m^{-1} here assigned to ¹⁶OH, and the corresponding line at 353760 m⁻¹ assigned to ¹⁸OH⁻ similarly almost coincides with our line of ¹⁸OH at 353710 m⁻¹, the wavenumbers of the lines of 16OD- at 262250 and 261950 m⁻¹ and of $^{18}\text{OD}^-$ at 260400 m⁻¹ seem distinctly different from those of our lines at 261610 m⁻¹ of ¹⁶OD and 260030 m^{-1} of ¹⁸OD. It seems that these assignments to the anions are not contradicted by the present experiments. In fact, these assignments, based on only small displacements of wavenumbers from the gaseous phase to an argon matrix, tend to support our assignments for OH as well as to confirm that our lines are not due to OH⁻. However, the doubling of the lines, attributed [26] to site effects, for each of ¹⁶OH⁻ and ¹⁶OD⁻ but for neither ¹⁸OH⁻ nor ¹⁸OD⁻ remains unexplained. In the case of the lines here assigned to the OH radical, the fact that there is but a single sharp line for each isotopic variant raises no question of multiple types of trapping site, possible aggregation or association with other than surrounding argon.

In conclusion, the evidence that we present here demonstrates that we have for the first time observed and characterized by their infrared spectral lines hydroxyl radicals isolated in a matrix of a noble gas. In principle, rotational fine structure instead of a single line of each isotopic species could make more nearly definitive our assignments, but such fine structure for OH, as for OH⁻ [26], is lacking. It is possible that the lines at 345230 and 342800 m⁻¹ previously assigned [6] to OH, accepted without question by Suzer and Andrews [26], may be due to the hydroxyl radical in a complex with either H₂O, or one Ar atom [27]. Further information about the latter interaction could result from experiments on supersonic beams from free expansion, or from calculations of the potential energy like those recently reported for OH+He and OH+Ne [28].

Acknowledgement

We thank the Chemical Manufacturers Association (USA) and the National Science Council of the Republic of China for support of this research. JFO also thanks Professor B.A. Thrush, F.R.S., of the University of Cambridge for his earlier suggestions about the mechanism of OH production.

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