equal to $^1/_9k_{\mathrm{diff}}$ and a quantitative singlet oxygen yield (eq 4a).

$$^3\mathrm{S}^* + {}^3\mathrm{O}_2 \xrightarrow{(1/9)k_{\mathrm{diff}}} {}^1(\mathrm{S}^*,\mathrm{O}_2) \rightarrow {}^1\mathrm{S}_0 + {}^1\mathrm{O}_2^* \qquad (4a)$$

$$\xrightarrow{(1/3)k_{\mathrm{diff}}} {}^3(\mathrm{S}^*,\mathrm{O}_2) \rightarrow {}^1\mathrm{S}_0 + {}^3\mathrm{O}_2 \qquad (4b)$$

$$\xrightleftharpoons{(5/9)k_{\mathrm{diff}}} {}^5(\mathrm{S}^*,\mathrm{O}_2) \qquad (4c)$$

On the other hand, the spin exchange and charge-transfer interactions are associated with $k^{\mathrm{T}}_{\mathrm{q,O_2}}$'s approaching $^1/_3k_{\mathrm{diff}}$ and reflect themselves into less than quantitative $^1\mathrm{O}_2^*$ yields (eq 4b). For the present triplet systems, the observed $k^{\mathrm{T}}_{\mathrm{q,O_2}}$'s are all close to $^1/_9k_{\mathrm{diff}}$, suggesting the dominance of energy transfer. The latter is also indicated by the triplet sensitized $^1\mathrm{O}_2^*$ yields ($\phi_{\mathrm{T}}^{\Delta}$) being high (close to unity in the case of **3**).

The rate constants for quenching by the stable free radical, DTBN, follow a trend opposite to that observed for oxygen quenching (Table II). The large value of $k^{\mathrm{T}}_{\mathrm{q,DTBN}}$ for **2** is not surprising, because aromatic triplets with E_{T}'s > 42 kcal mol^{-1} are quenched by nitroxy radicals by an energy transfer mechanism[43] (eq 5c) with $k^{\mathrm{T}}_{\mathrm{q}}$ reaching the limit of diffusion control at

$$^3\mathrm{S}^* + {}^2\mathrm{R} \longrightarrow {}^4(\mathrm{S}^*,\mathrm{R}) \longrightarrow {}^1\mathrm{S}_0 + {}^4\mathrm{R}^* \qquad (5a)$$

$$\begin{array}{lll} \longrightarrow {}^2(\mathrm{S}^*,\mathrm{R}^*) & \longrightarrow {}^1\mathrm{S}_0 + {}^2\mathrm{R} & (5b) \\ & \searrow & \\ & \quad {}^1\mathrm{S}_0 + {}^2\mathrm{R}^* & (5c) \end{array}$$

$E_{\mathrm{T}} \sim 60$ kcal mol^{-1}. By the same token, the fact that $k^{\mathrm{T}}_{\mathrm{q,DTBN}}$'s for **1** and **3** are well below the limit of diffusion control points to the structural distortion in the triplets of these systems. However, we note that $k^{\mathrm{T}}_{\mathrm{q,DTBN}}$'s for **1** and **3** are much higher than for a structurally rigid aromatic triplet with E_{T} comparable to the available vertical energies of the relaxed triplets of **1** and **3** (e.g., $k^{\mathrm{T}}_{\mathrm{q,DTBN}} = (5-9) \times 10^6$ M^{-1} s^{-1} for triplets of anthracenes in benzene).[44] Again, in the spin exchange mechanism of quenching (eq 5b), the torsional distortion plays an important role in enhancing the bimolecularly induced radiationless process.

In the "chemical" quenching of triplets by TEA and *p*-methoxyphenol, **2** proves to be far more reactive than **1** and **3**. The difference is too large to be explained in terms of a steric effect in electron or hydrogen-atom transfer to the carbonyl triplets. The lowering of available triplet energy as a result of structural distortion in **1** and **3** results in the decrease of their reduction potential (excited-state) and makes them poor acceptors in charge-transfer interactions.

Finally, we note that Ishibe and Yutaka[4] ruled out the intermediacy of triplets in the photorearrangement of hindered 4-pyrones to 2-pyrones (Scheme I) on the basis of the lack of effect of dienes (*trans*- and *cis*-piperylenes) on photorearrangement quantum yields. Our time-resolved study shows that the triplets of hindered 4-pyrones can be short-lived and that the rate constants for their quenching by a diene can be small. Specifically, for **1** at 1–4 mM, the $k^{\mathrm{T}}_{\mathrm{q}}\tau^{\mathrm{T}}$ values with *trans*-piperylene as the quencher are calculated to be 6.7–7.5 M^{-1}. At the diene concentrations (0.15–0.20 M) used by Ishibe and Yutaka,[4] these $k^{\mathrm{T}}_{\mathrm{q}}\tau^{\mathrm{T}}$ values should result in ≥50% suppression of triplet-mediated photochemistry. Since no such large reduction in photorearrangement yields has been noted, the conclusion[4] regarding the lack of triplet participation remains valid. At the same time, this rules out the photorearrangement as a possible reason for the intrinsic short triplet lifetime of **1**.

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[40] (a) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708–720. (b) Stevens, B. *J. Phys. Chem.* **1981**, *85*, 3555–3557.

[41] Garner, A.; Wilkinson, F. In *Singlet Oxygen*, Ranby, B., Rabek, J. F., Eds.; Wiley: New York, 1978; p 48. Garner, A.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *45*, 432–435.

[42] Saltiel, J.; Thomas, B. *Chem. Phys. Lett.* **1976**, *37*, 147–148.

[43] (a) Kuzmin, V. A.; Tatikolov, A. S. *Chem. Phys. Lett.* **1978**, *53*, 606–610. (b) Watkins, A. R. *Chem. Phys. Lett.* **1980**, *70*, 262–265. (c) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 727–737. (d) Kuzmin, V. A.; Tatikolov, A. S.; Borisevich, Yu. E. *Chem. Phys. Lett.* **1978**, *53*, 52–55.

[44] Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem.* **1984**, *26*, 39–47.

Isotopic Exchange in the Sonolysis of Aqueous Solutions Containing $^{14,14}\mathrm{N}_2$ and $^{15,15}\mathrm{N}_2$

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(Received: April 14, 1986)

Water was irradiated with 300-kHz ultrasonic waves under an atmosphere of argon and molecular nitrogen, the nitrogen being a 1/1 mixture of $^{14,14}\mathrm{N}_2$ and $^{15,15}\mathrm{N}_2$. Maximum yields of the nitrogen-containing products, $^{14,15}\mathrm{N}_2$, $\mathrm{NO_2^-}$, $\mathrm{NO_3^-}$, $\mathrm{NH_3}$, and $\mathrm{N_2O}$, were observed for $\mathrm{N_2}$ concentrations between 40% and 60% in the gas atmosphere. The $^{14,15}\mathrm{N}_2$ yield was almost as large as that of $\mathrm{NO_2^-} + \mathrm{NO_3^-}$, while $\mathrm{NH_3}$ and $\mathrm{N_2O}$ were present in much smaller amounts. The yields of $\mathrm{H_2O_2}$, $\mathrm{H_2}$, and $\mathrm{O_2}$ were largest in the absence of $\mathrm{N_2}$ and continuously decreased with increasing $\mathrm{N_2}$ concentration. It is proposed that isotopic nitrogen exchange is a process accompanying the redox processes between O atoms, OH and H radicals, and nitrogen molecules.

Introduction

For many years it has been known that nitrous acid and nitric acid are formed when aerated water is exposed to ultrasonic waves sufficiently intense to produce cavitation.[1-4] The formation of these products may occur in a similar way as that of nitrogen oxides in the combustion of fuels with air, as high temperatures of several thousand kelvin exist in the final stage of the compression phase of the oscillating or collapsing cavitation bubbles.[6-7] At these high temperatures, H and OH radicals are formed from water[8] and oxygen atoms from oxygen.[9] The present study on

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[1] Beuthe, H. *Z. Phys. Chem., Abt. A* **1933**, *163A*, 161.

[2] Polotzki, I. G. *J. Gen. Chem. USSR (Engl. Transl.)* **1947**, *17*, 649.

[3] Virtanen, A. J.; Ellfolk, N. *J. Am. Chem. Soc.* **1950**, *72*, 1046.

[4] Mead, L.; Sutherland, R. G.; Verrall, R. E. *Can. J. Chem.* **1976**, *54*, 1114.

[5] Noltingk, B. E.; Neppiras, E. A. *Proc. Phys. Soc., London, B* **1950**, *B63*, 674.

[6] Fitzgerald, M. E.; Griffing, V.; Sullivan, J. *J. Chem. Phys.* **1956**, *25*, 926.

[7] Flynn, H. G. In *Physical Acoustics*; Mason, W. P., Ed.; Academic: New York, 1964; Vol. IB, Chapter 9.

0022-3654/86/2090-5989$01.50/0

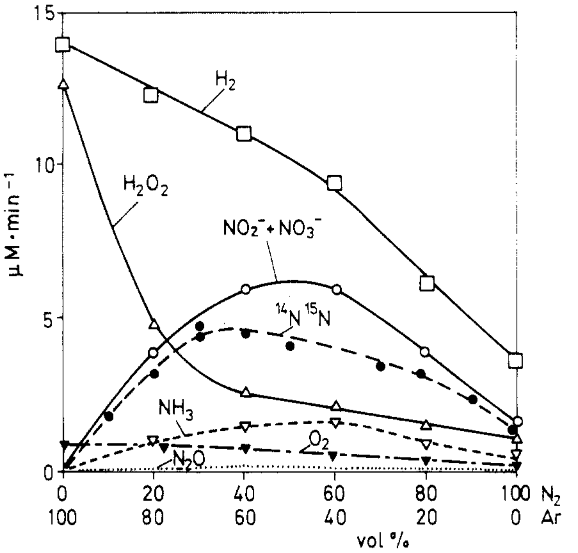

Figure 1. Rate of formation of various products as a function of the concentration of N_2 in the argon–nitrogen atmosphere. Insonation time was 40 min. Rates are overall rates.

$^{14}N^{15}N$ formation in water containing nitrogen in the form of a 1/1 mixture of $^{14,14}N_2$ and $^{15,15}N_2$ was undertaken to trace nitrogen atoms as intermediates and to understand the mechanism of NO_2^- and NO_3^- formation in more detail. Isotopic exchange reactions in the sonolysis of the systems D_2–H_2O[10] and $^{18,18}O_2$–$H_2{}^{16}O$[11] have recently been shown to occur with rather high yields, free radicals, and atoms being the intermediates in these processes.

Experimental Section

The 300-kHz quartz generator and the insonation vessel were described previously.[10] The vessel had a total volume of 66.5 cm^3 and could be closed during insonation. Water (37.5 cm^3) was insonated under an atmosphere consisting of argon and nitrogen, the nitrogen being a 1/1 mixture of $^{14,14}N_2$ and $^{15,15}N_2$. Deaeration of the water and saturation with the desired gas mixture as well as the final collection of the gas were made with standard Van Slyke and syringe techniques.[12] The isotopic composition of nitrogen and nitrous oxide was determined by combined gas chromatography and mass spectrometry. H_2 and O_2 were determined gas chromatographically and NH_3, NO_2^-, and NO_3^- with an ion chromatograph. H_2O_2 was measured spectrophotometrically by using titanyl sulfate.

Results

Figure 1 shows the rate of formation of various products as a function of the volume percent of N_2 in the nitrogen–argon atmosphere under which water was irradiated. The nitrogen was a 1/1 mixture of the two isotopic N_2 molecules.

In the absence of N_2, hydrogen, hydrogen peroxide, and oxygen are the products. Their yields continuously decrease as the concentration of N_2 increases, the initial decrease in the yield of H_2O_2 being much steeper than that of H_2. The O_2 yield, which was rather low, decreased relatively little. The yields of the N-containing products, i.e., $^{14,15}N_2$, NO_2^- + NO_3^-, NH_3, and N_2O, had maximum values at nitrogen concentrations between 40% and 60%. NO_2^- was formed in greater yield than NO_3^-.

We now consider the material balance and the yields of decomposed water and nitrogen molecules. Under pure argon, 14 μM H_2, 13 μM H_2O_2, and 1 μM O_2 were formed per minute, which corresponds to the rate of decomposition of water molecules of 28 μM·min^{-1} according to the overall equations

$$2H_2O \rightarrow H_2 + H_2O_2 \qquad (1)$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (2)$$

The material balance at 50 vol % N_2 in the atmosphere is calculated as follows. The yields of 2μM NH_3, 3 μM H_2O_2, 0.8 μM O_2, 6 μM HNO_2 + HNO_3, and 10.5 μM H_2 per minute correspond to the conversion of 39 μM·min^{-1} H atoms and 19.6 μM·min^{-1} O atoms, or a decomposition rate of 19 μM·min^{-1} of water molecules. The rate of decomposition of water molecules in an argon–nitrogen (1/1) bubble is about one-third lower than in a pure argon bubble. From the yields of the N-containing products at 50 % N_2, using twice the yield of $^{14,15}N_2$ to account for the reformation of $^{14,14}N_2$ and $^{15,15}N_2$ in the isotopic scrambling, a yield of 17 μM·min^{-1} of converted N atoms or 8.5 μM·min^{-1} of initially decomposed nitrogen molecules is calculated. It is concluded that twice as many water molecules as nitrogen molecules are decomposed in an argon–nitrogen (1/1) bubble.

The maximum rate of N_2O formation was 0.2 μM·min^{-1} at 40% N_2; this yield includes the yields of all three isotopic N_2O molecules. The ratios in which these isotopic forms were present was 1:1:1; i.e., the mixed isotopic species $^{14,15}N_2O$ was not twice as abundant as the $^{14,14}N_2O$ and $^{15,15}N_2O$ species, as would be expected from statistical isotope scrambling. Nitrous oxide is known to decompose when it is present in small amounts in an argon atmosphere under which water is irradiated.[13] The very low yield in Figure 1 is perhaps due to partial decomposition during irradiation. To demonstrate the decomposition of N_2O, experiments were carried out with a mixture of $^{15,15}N_2$ (90%) and $^{14,14}N_2O$ (10%). The main product was $^{14,14}N_2$; its yield was 330 μM·min^{-1}, i.e., very much higher than the yields observed in the experiments of Figure 1. NO_2^- and NO_3^- were also formed in much higher yields than in Figure 1. A more detailed study on N_2O decomposition by ultrasonic irradiation is described in a succeeding paper.[14]

The experiments of Figure 1 were also carried out with Ar–N_2 mixtures to which 10% H_2 was added. The yields of the main products, i.e., H_2O_2, NO_2^- + NO_3^-, and $^{14,15}N_2$ were smaller by a factor of 2–3 than in the absence of H_2. The yields of the minor products, i.e.; NH_3 and N_2O, were not analyzed in these experiments.

Discussion

When aqueous solutions are irradiated under an atmosphere of argon and a second gas, which is diatomic or triatomic and undergoes chemical reaction, a maximum in the yield vs. added gas concentration curves is often observed.[9–11,13,15] This is understood in terms of two opposing effects. With increasing concentration of the second gas, the yield increases as this gas is a reactant. On the other hand, the temperature in adiabatically compressed gas bubbles becomes lower if the second gas has a lower ratio of specific heats than argon. The maxima of the yields of the nitrogen-containing products in Figure 1 are explained in this way.

The continuously decreasing yields of H_2O_2 and H_2 are explained by an interference of nitrogen with the formation of these products. Under pure argon, a fraction of the radicals from water decomposition

$$H_2O \rightarrow H + OH \qquad (3)$$

re-form water[9,10,13] and partially combine to form the final products, H_2 and H_2O_2

$$2H \rightarrow H_2 \qquad (4)$$

$$2OH \rightarrow H_2O_2 \qquad (5)$$

In a recent study[11] on the isotopic exchange in the system $^{18,18}O_2$–$H_2{}^{16}O$ we concluded that OH radicals and O atoms are

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(8) Makino, K.; Mossoba, M. M.; Riesz, P. *J. Phys. Chem.* **1983**, *87*, 1369.

(9) Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1985**, *89*, 4342.

(10) Fischer, Ch.-H.; Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1986**, *90*, 222.

(11) Fischer, Ch.-H.; Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1986**, *90*, 1954.

(12) Hart, E. J.; Thomas, J. K. Report ANL-7856, Argonne National Laboratory, Argonne, IL, 1971.

(13) Henglein, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 100.

(14) Hart, E. J.; Henglein, A. *J. Phys. Chem.*, following paper in this issue.

(15) Henglein, A. *Naturwissenschaften* **1956**, 277, 278; **1957**, 179.

interconvertible in the hot gas bubbles

$$2OH \rightleftharpoons O + H_2O \qquad (6)$$

and that the radical combinations 4 and 5, as well as 7

$$2O \xrightarrow{M} O_2 \qquad (7)$$

take place in cooler parts of the interfacial region. The fact that the H_2O_2 yield decreases more rapidly than that of H_2 is taken as an indication for nitrogen acting as a better scavenger for O atoms and OH radicals than H atoms. The reactions of OH radicals and O atoms with N_2 are known from combustion chemistry and shock-tube studies:[16,17]

$$OH + {}^{15}N_2 \rightarrow {}^{15}N_2O + H$$
$$5 \times 10^{-12}e^{-40\,400/T} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \qquad (8a)$$

$$OH + {}^{14}N_2 \rightarrow {}^{14}N_2O + H \qquad (8b)$$

$$O + {}^{14}N_2 \xrightarrow{M} {}^{14}N_2O$$
$$3.9 \times 10^{-35}e^{-10\,400/T} \text{ molecule}^{-2} \text{ cm}^6 \text{ s}^{-1} \qquad (9a)$$

$$O + {}^{15}N_2 \xrightarrow{M} {}^{15}N_2O \qquad (9b)$$

$$O + {}^{14,14}N_2 \rightarrow {}^{14}NO + {}^{14}N \qquad (10a)$$

$$O + {}^{15,15}N_2 \rightarrow {}^{15}NO + {}^{15}N$$
$$1.3 \times 10^{-10}e^{-38\,000/T} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \qquad (10b)$$

At high temperatures, reactions 8–10 have comparable rates. Reactions 8 and 9 explain the formation of N_2O. Nitrous oxide is thermally decomposed according to

$$N_2O \xrightarrow{M} N_2 + O \qquad 8.3 \times 10^{-10}e^{-29\,000/T} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \qquad (11)$$

$$O + N_2O \rightarrow 2NO$$
$$1.7 \times 10^{-10}e^{-14\,100/T} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \qquad (12)$$

$$O + N_2O \rightarrow N_2 + O_2$$
$$1.7 \times 10^{-10}e^{-14\,100/T} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \qquad (13)$$

which explains why little N_2O was found. The decomposition of N_2O is dealt with in more detail in a succeeding paper.[14] Reactions 10 and 12 produce NO as an intermediate, and this explains the formation of HNO_2 and HNO_3 as NO may be further oxidized by O or OH. The formation of $^{14,15}N_2$ could occur through the combination of the nitrogen atoms formed in reactions 10a,b. However, it seems more probable that the nitrogen atoms react with NO

$${}^{14}N + {}^{15}NO \rightarrow {}^{14,15}N_2 + O \qquad (14)$$

This reaction requires no activation energy, has a rate constant of 2.7×10^{-11} molecule^{-1} cm^3 s^{-1}, and occurs at almost every collision. We also do not postulate a significant contribution of an exchange reaction between N atoms and N_2 molecules. This reaction has not been found in experiments where the temperature was varied up to 1000 °C.[18] If it occurred to a noticeable degree under our conditions, a larger $^{14,15}N_2$ yield would be expected because of the chain nature of this reaction.

We attribute the decrease in H_2 yield to NO, which also acts as an efficient scavenger for H atoms

$$H + NO \rightarrow N + OH \qquad (15)$$

The rate constant is $3.6 \times 10^{-10}e^{-8710/T}$ molecule^{-1} cm^3 s^{-1}. However, the fact that NH_3 is formed in small yields shows that somehow H atoms are reactive toward nitrogen as was already observed in sonolysis experiments on NH_3 formation in aqueous solutions containing both N_2 and H_2.[19] It seems that a reaction of H atoms with N_2 has not yet been observed in combustion chemistry.

Small amounts of molecular hydrogen in the gas atmosphere decreased the yields of all main products, i.e., NO_2^-, NO_3^-, and $^{14,15}N_2$. This effect is also understood in terms of reactions 8–10 as the oxidizing species OH and O are very reactive toward H_2.

The formation of N_2O is explained by reactions 8 and 9 in the above mechanism. These reactions lead to $^{15,15}N_2O$ and $^{14,14}N_2O$. The fact that $^{14,15}N_2O$ was also formed has to be explained by an additional process that leads to N_2O. A possible reaction is[17]

$$NO + NO \rightarrow N_2O + O$$
$$2.2 \times 10^{-12}e^{-32\,100/T} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \qquad (16)$$

Since the homoisotopic and mixed isotopic forms of N_2O are produced in different reactions, it is understandable that the ratio of abundance of 1:2:1 expected from statistical isotopic scrambling was not found.

The time during which chemical reaction in a compressed gas bubble can take place may be deduced from the observations in sonoluminescence studies. The luminescence occurs in short flashes of about 10^{-7} s duration at the maximum compression of oscillating or collapsing gas bubbles.[20,21] In the earlier investigations on sonoluminescence, temperatures in the hot gas bubbles of 5000 K or even higher have been postulated,[20,22] while the more recent studies led to the conclusion that the temperatures are only in the 1500–2500 K range.[23,24] The reaction of an atom or radical with a gas molecule would efficiently occur if the reaction time is 10^{-7} s or shorter. The concentration of gas molecules in a bubble compressed to 100 bar is of the order of 1 M, and, under these conditions, the rate constant should exceed 10^7 M^{-1} s^{-1} if a reaction is to occur with a good yield. The specific rate of reaction 10, which is crucial for isotopic exchange, exceeds 10^7 M^{-1} s^{-1} at temperatures above 4000 K.[16] Our chemical rate considerations thus lead us to the conclusion that temperatures of many 1000 K indeed exist in the hot gas bubbles. The lower temperatures derived from the luminescence studies possibly are understood in terms of the luminescence being emitted from excited species in the interface.

Acknowledgment. We thank H. Pohl for excellent assistance in the analytical work. The support of the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. N_2, 7727-37-9; H_2O, 7732-18-5.

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(16) Hanson, R. K.; Salimian, S. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer: New York, 1984; Chapter 6.

(17) Hampson, R. F.; Garvin, D. "Reaction Rate and Photochemical Data for Atmospheric Chemistry"; National Bureau of Standards Special Publication 513, Gaithersburg, MD, 1978.

(18) Back, R. A.; Mui, J. Y. P. *J. Chem. Phys.* **1962**, *66*, 1362.

(19) Sokol'skaya, A. V.; El'piner, I. E. *Akust. Zh.* **1957**, *3*, 293.

(20) Günther, P.; Heim, E.; Schmitt, A.; Zeil, W. *Z. Naturforsch., A: Astrophys., Phys., Phys. Chem.* **1957**, *12A*, 521.

(21) Günther, P.; Heim, E.; Eichkorn, G. *Z. Angew. Phys.* **1959**, *11*, 274.

(22) Srinivasan, D.; Holroyd, L. V. *J. Appl. Phys.* **1961**, *32*, 446.

(23) Young, F. R. *J. Acoust. Soc. Am.* **1976**, *60*, 100.

(24) Sehgal, C.; Steer, R. P.; Sutherland, R. G.; Verrall, R. E.; *J. Chem. Phys.* **1979**, *70*, 2242.