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Xenon-129 NMR and the Thermodynamic Parameters of Xenon Hydrate†

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From calorimetry-assisted determination of the overall composition of xenon hydrate and the relative degree of occupancy of the two kinds of hydrate cavities given by the proton-decoupled ^{129}Xe NMR spectrum, the absolute occupancies of the two cavity types have been determined under three-phase equilibrium conditions (0 °C and 1.55 bar). In terms of the ideal solid solution theory of clathrate stability, the chemical potential of the water molecules in the empty hydrate lattice is greater than that of ice by (1297 ± 110) J/mol at 0 °C and 1 bar for this simplest of structure I hydrates. The thermodynamic parameters are discussed, as are conditions which affect the reliability of NMR measurement of relative abundance.

It is almost 30 years since the statistical thermodynamic theory of ideal localized adsorption on surfaces was adapted[1,2] to the three-dimensional solid solutions of the kind that characterize gas hydrates and other clathrates. With the help of certain simplifying assumptions—the most important being that guest–guest interactions are negligible and that the host lattice is not distorted by the presence of guest molecules—the chemical potential of the water molecules in a structure I hydrate is given by

$$\mu_w(h) - \mu_w(h^0) = \frac{RT}{23}[3 \ln (1 - \theta_L) + \ln (1 - \theta_S)] \quad (1)$$

where $\mu_w(h^0)$ is the chemical potential of water molecules in the lattice with empty cavities and θ_L and θ_S are the extents of occupancy of the large and small cavities. Under conditions where the hydrate exists in equilibrium with ice, the left side of eq 1 becomes $\mu_w(\text{ice}) - \mu_w(h^0) = -\Delta\mu_w{}^0$, where $\Delta\mu_w{}^0$ is the chemical potential of the empty hydrate lattice relative to ice. Since the degree of occupancy of the two kinds of cages will not in general be the same, one cannot generally derive $\Delta\mu_w{}^0$ from measurements of the composition, which depends on $3\theta_L + \theta_S$. Most estimates of $\Delta\mu_w{}^0$ have been based on assumptions about the potential functions describing guest–host molecule interactions which have been used to derive Langmuir constants for the two cages and thus to estimate cage occupancies at pressures corresponding to equilibrium among hydrate, ice (or liquid water), and gas phases. In some gas hydrates the guest molecules may be taken to be too large to occupy any of the small cages ($\theta_S = 0$). In such cases $\Delta\mu_w{}^0$ can be directly determined from the composition. This method has been applied by Dharmawardhana et al.[3] to cyclopropane hydrate.

Here we take advantage of the presence in the ^{129}Xe NMR spectrum of xenon hydrate[4] of well-resolved lines from xenon atoms in the large and small cavities to determine the relative values of θ_L and θ_S. The overall composition of the same xenon hydrate sample is found by an analysis which makes use of a recently developed technique[5] in which any excess water present is detected calorimetrically as ice.

Since argon and krypton hydrates have been shown[6] to be type II hydrates, xenon hydrate is the only type I hydrate in which the guest–host interactions are simplified by the presence of a monatomic guest species. Moreover, the dissociation pressure of xenon hydrate is low enough (1.55 bar at 0 °C) that compressibility effects may be ignored.

Experimental Methods

Xenon hydrate samples for both calorimetric and NMR studies were prepared from powdered ice and xenon gas in a rotatable reaction vessel equipped with a Setra transducer (Model 204) for pressure measurement and with stainless steel rods for intermittent grinding of the sample. The "equilibrium" hydrate was cycled between 263 and 272 K over 5 days, after which the xenon gas pressure was 4 bar. The pressure was reduced to 2 bar and the vessel kept in an ice bath for 3 days. Final conditioning was at the equilibrium pressure of 1.545 ± 0.005 bar. A sample prepared under excess xenon pressure (20 bar at −20 °C) was also subjected to calorimetric[5] and NMR examination.

Two additional samples of xenon hydrate, designed to contain ice to ensure hydrate–ice–gas equilibrium, were prepared for NMR study from excess powdered ice and liquid xenon sealed in a 10-mm-o.d. sample tube at low temperatures, stored in a freezer, and then conditioned near 0 °C for several days. A mixed hydrate of xenon and ethylene oxide was made by grinding a frozen EO–water solution, adding liquid xenon, and conditioning at −13 °C for several weeks. The water:xenon:EO mole ratio was about 13:1:1.

^{129}Xe spectra were recorded at 49.8 MHz with a Bruker CXP NMR spectrometer by two methods. The first was the standard Fourier transform method in which single pulses were applied to the sample and the free induction decays (fids) were digitized under conditions of high-power proton decoupling; the sweep width was 50 kHz for 1024-point fids with zero filling to 4096 points before Fourier transformation. Because long ^{129}Xe spin–lattice relaxation times necessitated long delays between pulses, the potentially time-saving polarization transfer method was also studied. The ^{129}Xe–^{1}H cross-polarization dynamics were followed by recording peak areas as a function of cross-polarization time with a radio-frequency field amplitude of 30 kHz and times between successive pulses of 1 min at a number of temperatures above 200 K and 3 min at 77 K.

The composition of the hydrate was determined as described elsewhere.[5] Briefly, the cold sample was transferred to the calorimeter and then heated through 0 °C under a pressure of xenon gas larger than the hydrate dissociation pressure to determine calorimetrically the amount of ice present. This was always less than 1%; some samples were further conditioned under excess xenon pressure until ice was no longer detected. The sample was then cooled to 78 K with gradual removal of gas-phase xenon, and hydrate was decomposed by heating to room temperature. The amount of gas released was determined by *P–V–T* measurements; the water present after hydrate decomposition was determined calorimetrically as ice and by weight, with good agreement.

Results and Discussion

NMR Spectra. Figure 1 shows an earlier ^{129}Xe spectrum recorded for an equilibrium xenon hydrate prepared with D_2O

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† Issued as NRCC No. 26409.

(1) Barrer, R. M.; Stuart, W. I. *Proc. R. Soc. London, Ser. A* **1957**, *A242*, 172.

(2) Van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.

(3) Dharmawardhana, P. B.; Parrish, W. R.; Sloan, E. D. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 410.

(4) Ripmeester, J. A.; Davidson, D. W. *J. Mol. Struct.* **1981**, *75*, 67.

(5) Handa, Y. P. *J. Chem. Thermodyn.*, in press.

(6) Davidson, D. W.; Handa, Y. P.; Ratcliffe, C. I.; Tse, J. S.; Powell, B. M. *Nature (London)* **1984**, *311*, 142.

0022-3654/86/2090-6549$01.50/0

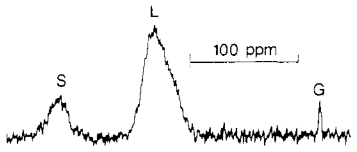

Figure 1. ^{129}Xe NMR spectrum of xenon deuteriohydrate at 275 K. The peaks are from xenon in the small (S) and large (L) cages and in the gas phase (G). Recorded from 24 fids at intervals of 800 s.

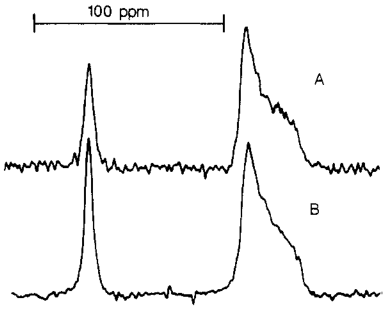

Figure 2. (A) ^{129}Xe proton-decoupled spectrum of xenon hydrate at 275 K. Recorded from 16 fids at 900-s intervals. (B) ^{129}Xe proton-decoupled cross-polarized spectrum of xenon hydrate at 265 K. Recorded from 24 fids at 60-s intervals with a CP time of 500 μs.

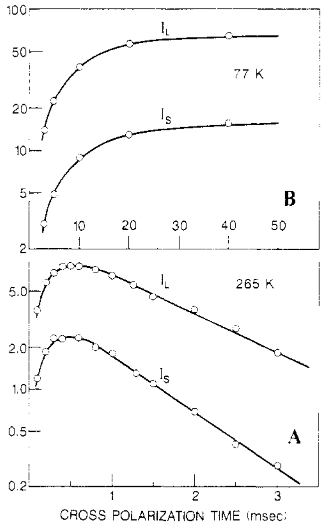

Figure 3. Dependence of relative integrated intensities (arbitrary units) of ^{129}Xe lines from atoms in large (I_L) and small (I_S) cages on cross-polarization time at two temperatures.

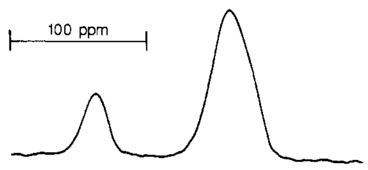

Figure 4. ^{129}Xe cross-polarization spectrum of xenon hydrate at 77 K. Recorded from four fids at 180-s intervals with a CP time of 40 ms.

TABLE I: Values of Equilibrium Hydration Number *n* of Xenon Hydrate near 0 °C

authors (ref)	$\Delta H(\mathrm{h} \rightarrow \mathrm{l}_1 + \mathrm{g})$/(J/mol)	n
	Indirect Method	
de Forcrand (22)	76 425	8.49
Braun (23)	70 290 ± 2090	7.47 ± 0.38
Aaldijk (11)	61 670 ± 840	6.03 ± 0.17
Ewing and Ionescu (12)	63 460 ± 2090	6.33 ± 0.38
Berecz and Balla-Achs(24)	72 930	7.91
	Direct Methods	
Braun (23)		6.39, 6.48, 6.59
Barrer and Edge (10)		6.05–6.25 (below 0 °C)
Aaldijk (11)		6.06
Cady (25)		6.48
this work		6.286 ± 0.030

to reduce the broadening effects of interactions with protons.[4] Because of the long ^{129}Xe spin–lattice relaxation time [$T_1(^{129}\mathrm{Xe})$], it took 5 h to record this spectrum. From the relative intensities of the peaks in this and similar spectra, a ratio of cage occupancy θ_S/θ_L of 0.77 ± 0.02 was estimated. Note that there are 3 times as many large as small cages in structure I hydrates.

Narrower and therefore improved spectra were obtained for the H_2O hydrate with high-power proton decoupling (Figure 2A), but again because of large $T_1(^{129}\mathrm{Xe})$ values, the time required remained long. With the aid of cross polarization (CP), Figure 2B was recorded in one-tenth of the time, primarily because much shorter T_1(H) values for protons make possible a faster pulse repetition rate.

A problem now arises, however, in the relative intensities of the lines from xenon in the small and large cages. Whereas numerous spectra recorded around 275 K with decoupling alone give $I_S/I_L = \theta_S/3\theta_L$ values close to 0.25, highly variable values of this ratio are found for the CP measurements. The reason for this behavior is seen in Figure 3A. The areas of the peaks from xenon in the large and small cages have a different dependence on cross-polarization time. The intensities are largest near 500 μs and thereafter decay at rates which are rapid and apparently different for the two kinds of cages. Similar behavior is observed for CP measurements at other temperatures between 245 and 275 K. The rapid decay of cross polarization depends on the presence of small values of $T_{1\rho}$(H), the proton spin–lattice relaxation time in the rotating frame. The dielectric relaxation times of the water molecules in xenon hydrate[7] (e.g., τ_c = 30 μ_s at 265 K) are not much larger in this temperature range than correspond to $\omega_1\tau_c = 1$, and $T_{1\rho}$(H) values of the order of a millisecond are expected. Polarization curves like those shown in Figure 3A may formally be fairly accurately described in terms of a superposition of exponential growth and exponential decay, but the resulting parameters are not well enough defined to yield accurate relative concentrations of xenon in the two cage types.

At low temperatures $T_{1\rho}$(H) becomes very long and decay of ^{129}Xe polarization is not a problem. As shown in Figure 3B transfer of polarization at 77 K is complete after 50 ms, and the intensity ratio I_S/I_L is independent of CP time. For samples which are rapidly quenched so as not to disturb the high-temperature equilibrium state, the low-temperature CP measurements give the same cage occupancy ratio as measured by the proton decoupling method at higher temperatures.

The ^{129}Xe spectra of the H_2O hydrate confirm the shielding parameters previously reported[4] for the D_2O hydrate. Near 275 K the downfield "physical" shifts for molecules in the small and large cages average 242 and 152 ppm from the resonance of dilute xenon gas. (At 77 K the separation of the two peaks has increased to 100 ppm.) The anisotropy of the axially symmetric shielding tensor of xenon in the large ($\bar{4}2m$) cage is 32 ppm. The well-defined spectra of the H_2O hydrate show clearly the absence of asymmetry in the shape of the peak from xenon in the small cage. This cage has tetrahedral ($m3$) symmetry, and the shielding tensor is isotropic.

At low temperatures the resonance peaks maintain the same symmetries as at high temperatures but become 4 or 5 times as broad (Figure 4). The difference appears to be due to the difference in the reorientation rates of the water molecules in the two temperature regions. The low-temperature widths may be described by a Gaussian function with a value of β of about 8 ppm or 400 Hz. Below about 200 K the water-molecule reorientation rates[7] become much slower than 400 Hz and the 6-fold disorder in the orientations of each water molecule is "frozen in". The resonance peak then consists of contributions from xenon atoms in cages formed by water molecules with many distinct orientational configurations; symmetry is maintained by the space average

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(7) Garg, S. K.; Majid, Y. A.; Ripmeester, J. A.; Davidson, D. W. *Mol. Phys.* **1977**, *33*, 729.

TABLE II: Estimates of $\Delta\mu_w^\circ$ for Structure I Clathrate Hydrates at 0 °C and 1 bar

year	authors (ref)	method	$\Delta\mu_w^\circ$/ (J/mol)
1959	Van der Waals and Platteeuw (2)	composition of Br_2 hydrate	698 ± 17
1964	Child (26)	correlation of dissociation entropies with β-quinol clathrates	1254
1971	Aaldijk (11)	LJD model and dissociation pressures of Ar, Kr, and Xe hydrates	813
1972	Parrish and Prausnitz (13)	Kihara model and dissociation pressures of Xe and other hydrates	1262
1973	Davidson (19)	general fit of range of known compositions	1109 ± 63
1976, 1982	Holder (14), Holder and Hand (15)	Kihara potentials and dissociation pressures	1155
1980	Holder et al. (16)	Kihara potentials and dissociation pressures of Ar, Kr, and methane hydrates	1235 ± 10
1980	Dharmawardhana et al. (3)	composition of cyclopropane hydrate	1297 ± 98
1984	Holder et al. (20)	reevaluation of data of Dharmawardhana et al. (ref 3)	1299 ± 10
1985	John et al. (17)	application of corresponding states to Kihara potentials	1120
1985	Barakhov et al. (18)	Kihara potentials and dissociation pressures of Ar, Kr, and methane hydrates	1291 ± 5
1986	this work	experimental evaluation of cage occupancies in Xe hydrate	1297 ± 110

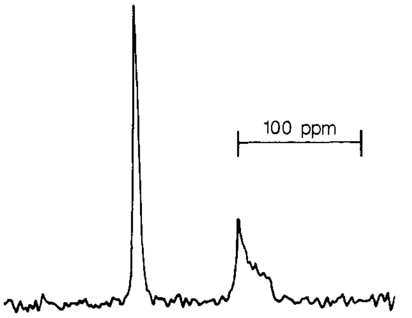

Figure 5. ^{129}Xe CP spectrum at 270 K of a hydrate with nearly equal amounts of encaged xenon and ethylene oxide. Recorded from 112 fids at 20-s intervals with a CP time of 500 μs.

over many cages. *Shielding of the xenon nucleus thus depends on the orientations of the water molecules as well as on their positions.* At relatively high temperatures the water-molecule reorientation rates are rapid enough to impose an identical time-averaged symmetry on all cages of the same kind, and this source of line broadening disappears.

The value of θ_S/θ_L for the hydrate in equilibrium with water and xenon gas at 273 K, based both on high-temperature decoupled spectra and CP spectra of samples rapidly quenched and measured at 77 K, is 0.73 ± 0.02. CP spectra of the hydrate prepared under excess pressure of xenon and quenched to 77 K gave 0.90 ± 0.03 for this ratio, a clear confirmation of the variable stoichiometry of the hydrate.

The mixed hydrate of ethylene oxide and xenon gave easily recorded spectra (Figure 5) which were characteristic of xenon in a structure I hydrate. A θ_S/θ_L value of about 4.4 was measured, with or without CP. T_1(H) is much smaller and $T_{1\rho}$(H) larger for the mixed hydrate because the presence of EO greatly accelerates the reorientation of water molecules. At 0 °C this reorientation time is about 0.03 μs in EO hydrate,[7] 3 orders of magnitude faster than in xenon hydrate. The relative intensities show that EO displaces Xe from the small cages much less than from the large. This is consistent with what is known about the (variable) composition of EO hydrate itself.[8] Thus, the composition EO·7.05H_2O for hydrate prepared at 8 °C in equilibrium with a 5.6 mol % aqueous solution of EO requires θ_S/θ_L for EO to be only about 0.32.

Hydrate Composition and the Value of $\Delta\mu_w^0$. The results from composition analyses of three samples gave hydration numbers of 6.280, 6.259, and 6.318. We take $n = 6.286 \pm 0.030$ at about the 90% confidence level for the equilibrium xenon hydrate at 0 °C and 1.55 bar.

From this composition and $\theta_S/\theta_L = 0.73 \pm 0.02$ for the same equilibrium hydrate, $\theta_L = 0.9809 \pm 0.0070$, $\theta_S = 0.7161 \pm 0.0161$, and $\Delta\mu_w^0 = 1297 \pm 110$ J/mol.

For structure I hydrates in which the guest molecules are so large that they may be assumed to occupy none of the small cages (an assumption difficult to prove), the above value of $\Delta\mu_w^0$ gives a limiting hydration number of 7.764 ± 0.037.

Comparison with Other Xenon Hydrate Compositions. A common method of determining gas hydrate compositions is the *indirect* method of Scheffer and Meyer[9] which gives the hydration number near 0 °C by division of the difference between the heats of hydrate dissociation into ice and gas $[\Delta H(\mathrm{h} \rightarrow \mathrm{I} + \mathrm{g})]$ and liquid water and gas $[\Delta H(\mathrm{h} \rightarrow \mathrm{l_l} + \mathrm{g})]$ by the heat of fusion of ice. The dissociation heats are commonly derived from the temperature dependences of the dissociation pressure curves at their point of intersection by use of the Clausius–Clapeyron equation, with small corrections for gas imperfection and solubility in water.

Barrer and Edge reported[10] $\Delta H(\mathrm{h} \rightarrow \mathrm{I} + \mathrm{g}) = 24\,142 \pm 84$ J/mol from a linear ln p vs. $1/T$ fit of six dissociation pressures between −62 and −5 °C. Aaldijk found[11] a value of 25 815 ± 410 J/mol from 31 dissociation pressure measurements between −10 and 0 °C; this author also found 24 112 ± 222 J/mol by reworking the data of Barrer and Edge. As will be reported elsewhere, the value given by direct calorimetric measurements in this laboratory is 25 430 ± 170 J/mol.

The available values of $\Delta H(\mathrm{h} \rightarrow \mathrm{l_l} + \mathrm{g})$ are all based on analysis of dissociation pressure measurements; they are summarized in Table I, along with indirect values of n obtained by taking $\Delta H(\mathrm{h} \rightarrow \mathrm{I} + \mathrm{g}) = 25\,430$ J/(mol of hydrate) and $\Delta H(\mathrm{I} \rightarrow \mathrm{l_l}) = 6008$ J/(mol of water). It is apparent that the error estimates given are generally significantly less than the true errors. Only the result of Ewing and Ionescu[12] is consistent with the present value of n and then only within a considerable range of uncertainty.

Direct measurements of hydrate compositions are known to be difficult, frequently because of the problem presented by the presence of excess water. None of the previous directly measured hydrate numbers listed in Table I agree well with the present value; the results of Barrer and Edge[10] come closest.

The present results, along with an equilibrium dissociation fugacity of 1.48 bar at 0 °C, give Langmuir constants for xenon in the small and large structure I cages of 1.70 ± 0.14 and 35 ± 13 bar^{-1} at this temperature. The first of these agrees with a value of 1.75 bar^{-1} which is obtained by extrapolating to 0 °C the value of the Langmuir constant measured below −5 °C by Barrer and Edge[10] for xenon in the small cage of the structure II hydrate of chloroform. It appears that the effects of the geometric differences between the small pentagonal dodecahedral cages of structures I and II (the symmetries are $m3$ and $\bar{3}m$, respectively) are not great.

Comparison with Previous Values of $\Delta\mu_w^0$. Table II gives values of $\Delta\mu_w^0$ which have been estimated previously for structure I hydrates. The limits of error are those assigned by the original authors. Most[11,13-18] of the estimates are based not on compositions

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(8) Glew, D. N.; Haggett, M. L. *Can. J. Chem.* **1968**, *46*, 3867.

(9) Scheffer, F. E. C.; Meyer, G. *Proc. Acad. Sci.* (*Amsterdam*) **1919**, *21*, 1104 and 1338.

(10) Barrer, R. M.; Edge, A. V. J. *Proc. R. Soc. London, Ser. A* **1967**, *A300*, 1.

(11) Aaldijk, L. Ph.D. Thesis, Technical University, Delft, 1971.

(12) Ewing, G. J.; Ionescu, L. G. *J. Chem. Eng. Data* **1974**, *19*, 367.

(13) Parrish, W. R.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11*, 26.

(14) Holder, G. D. Ph.D. Thesis, University of Michigan, 1976.

(15) Holder, G. D.; Hand, J. H. *AIChE J.* **1982**, *28*, 440.

(16) Holder, G. D.; Corbin, G.; Papadopoulos, K. D. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 282.

J. Phys. Chem. **1986**, *90*, 6552–6557

but on models of guest–host interaction (Lennard-Jones and Devonshire or Kihara potentials) in which there has been some force fitting of the interaction parameters to give agreement with experimental dissociation pressures, including those of the hydrates of argon and krypton which have been found[6] not to be structure I hydrates at all. Previous estimates based on compositions alone are free of such assumptions but are generally restricted to hydrates of large guest molecules where negligible occupancy of the small cages may be assumed. These include the results of van der Waals and Platteeuw,[2] who based their estimates on the composition of bromine hydrate which was erroneously assumed to be a structure I hydrate, of Davidson,[19] who attempted to find a value which was consistent with the range of compositions available in 1972 for structure I hydrates, and of Dharmawardhana et al.,[3] who measured the equilibrium composition of cyclopropane hydrate. The value of Holder et al.[20] is based on a reanalysis of Dharmawardhana's data.

The present value of 1297 ± 110 J/mol for xenon hydrate is in good agreement with other recent values for structure I hydrates. (We believe the error limits cited in ref 16, 18, and 20 to be greatly underestimated.) It is noteworthy that there appears to be no substantial difference between the chemical potentials of the water lattices which contain molecules as diverse as xenon (van der Waals radius 4.58 Å) and cyclopropane (5.84 Å).

Although the uncertainty is considerable, it is probable that there is some significance in the measurement of a somewhat larger value of θ_S/θ_L for xenon in the D_2O hydrate (0.77 ± 0.02) than in the H_2O hydrate (0.73 ± 0.02) near 0 °C. Hafemann and Miller found[21] that the dissociation pressure of xenon deuteriohydrate at −12.0 °C was 8% higher than for the hydrate. If this is true at 0 °C, use of the Langmuir constants found here for the hydrate predicts that θ_S/θ_L should be higher by 0.014 and $\Delta\mu_w{}^0$ by 30 J/mol for the deuteriohydrate than for the hydrate of xenon. Similar observations led to an estimate[21] that deuteriation of the water lattice increases $\Delta\mu_w{}^0$ by 25 J/mol for the type I hydrate of cyclopropane.

Registry No. Xenon hydrate, 60212-94-4; ^{129}Xe, 13965-99-6.

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[17] John, V. T.; Papadopoulos, K. D.; Holder, G. D. *AIChE J.* **1985**, *31*, 252.

[18] Barakhov, S. P.; Savvin, A. Z.; Tsarev, V. P. *Zh. Fiz. Khim.* **1985**, *59*, 1039.

[19] Davidson, D. W. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 2, p 115.

[20] Holder, G. D.; Malekar, S. T.; Sloan, E. D. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 123.

[21] Hafemann, D. R.; Miller, S. L. *J. Phys. Chem.* **1969**, *73*, 1398.

[22] de Forcrand, R. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1925**, *181*, 15.

[23] Braun, B. Dissertation, Bonn, 1938.

[24] Berecz, E.; Balla-Achs, M. *Gas Hydrates*; Elsevier: Amsterdam, 1983; p 176.

[25] Cady, G. H. *J. Phys. Chem.* **1983**, *87*, 4437.

[26] Child, W. C. *J. Phys. Chem.* **1964**, *68*, 1834.

Ketenyl Radical Yield of the Elementary Reaction of Ethyne with Atomic Oxygen at T = 290–540 K

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The ketenyl radical yield of the elementary reaction between ethyne and atomic oxygen was determined at T = 287 and 535 K, at a pressure of 2 Torr (He). Use was made of the flow reactor technique, in combination with molecular beam mass spectrometry. First, a detailed investigation was made of the kinetics of formation and destruction of HCCO in C_3O_2/H systems; by use of the absolute HCCO concentrations thus obtained, the sensitivity of the MBMS apparatus to HCCO could be determined. The HCCO yield of the elementary C_2H_2 + O reaction was then derived in C_2H_2/O systems from the observed stationary HCCO concentration and from the known HCCO destruction rate, at a given total C_2H_2 + O reaction rate. In this way, the HCCO yield of the elementary C_2H_2 + O reaction with 2σ error was found to be 59% ± 20% at 287 K and 64% ± 19% at 535 K.

Due to their importance in combustion chemistry, reactions of ethyne have since long been the subject of extensive studies. It has been shown that the reaction of ethyne with atomic oxygen proceeds via two important primary reaction channels:[1–4]

$$C_2H_2 + O \rightarrow CH_2 + CO \qquad \Delta H = -47 \text{ kcal mol}^{-1} \tag{1a}$$

$$C_2H_2 + O \rightarrow HCCO + H \qquad \Delta H = -19 \text{ kcal mol}^{-1} \tag{1b}$$

Past attempts to determine the relative importance of both reaction channels resulted in widely varying estimates for the branching ratio $0.1 \leqslant k_{1a}/k_1 \leqslant 0.97$.[2,4–6] In several recent studies, it was concluded that HCCO formation becomes important at elevated temperature[7,8] or at high collision energies,[9] while CH_2 production dominates at room temperature.[7] On the other hand, ab initio calculations without planarity constraints locate the transition states for both exit channels at nearly the same energy, about 10 kcal mol^{-1} below the barrier for the addition of O to C_2H_2;[10] since the transition state leading to CH_2 formation, involving a 1,2-H migration of the initial formylmethylene adduct, is expected to be tighter than that for C–H fissure, the ab initio results, in the framework of chemical activation RRKM theory,

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[1] Vinckier, C.; Schaekers, M.; Peeters, J. *J. Phys. Chem.* **1985**, *89*, 508.

[2] Williamson, D. G.; Bayes, K. D. *J. Phys. Chem.* **1969**, *73*, 1232.

[3] Kanofski, J. R.; Lucas, D.; Pruss, F.; Gutman, D. *J. Phys. Chem.* **1974**, *78*, 311.

[4] Vinckier, C.; Debruyn, W. *Symp. (Int.) Combust. [Proc.] 17th* **1979**, 623.

[5] Blumenberg, B.; Hoyermann, K.; Sievert, R. *Symp. (Int.) Combust. [Proc.] 16th* **1976**, 841.

[6] Williamson, D. G. *J. Phys. Chem.* **1971**, *75*, 4053.

[7] Löhr, R.; Roth, P. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 569.

[8] Aleksandrov, E. N.; Arutyunov, V. S.; Kozlov, S. N. *Kinet. Katal.* **1981**, *22*, 513.

[9] Clemo, A. R.; Duncan, G. L.; Grice, R. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1231.

[10] Harding, L. B. Annual Report Theoretical Chemistry Group, Argonne National Laboratory, 1984, p 3.

0022-3654/86/2090-6552$01.50/0