P_2O_5 powder. A cell of 24-cm path length equipped with polyethylene windows was used. The sample pressure was 40 torr. Interferograms were recorded 100 times, and the resolution was about 2 cm^{-1}. A broad band centered at 135 cm^{-1} with peaks at 133 and 120 cm^{-1} was observed.

A simulation of the envelope due to the skeletal torsional band for both conformers was made with program BC3[22] by using the rotational constants derived in Table V for $J \leq 99$. The gauche bands were calculated by assuming that the ratio of the intensities of the b-type and c-type bands was 1:2 by trial and error. The skeletal torsional mode for the trans conformer has a c-type band. This simulation showed that the two peaks were assignable to the c-type bands of both conformers and that the torsional bands were broadened by contributions from the b-type band of the gauche conformer and the overlapping hot bands. The best fit was obtained when the peak at 133 ± 2 cm^{-1} was assigned to the skeletal torsional band of the gauche conformer and 120 ± 2 cm^{-1} to that of the trans conformer. A comparison of the observed and best-fit theoretical spectra is shown in Figure 6. The uncertainty in the torsional frequencies, ±2 cm^{-1}, estimated from this simulation corresponds to that in the difference in the vibrational entropy, ΔS_{vib}, of ±0.016 cal/(mol K). Therefore, the total uncertainty in ΔH is estimated from that in ΔG, ±60 cal/mol, and from that in $T\Delta S_{vib}$, ±10 cal/mol, to be ±70 cal/mol.

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Registry No. 1-Chloropropane, 540-54-5.

Supplementary Material Available: Experimental data of the total intensity for 1-chloropropane obtained by gas electron diffraction (2 pages). Ordering information is given on any current masthead page.

The Equilibrium Reaction of the Luminol Radical with Oxygen and the One-Electron-Reduction Potential of 5-Aminophthalazine-1,4-dione

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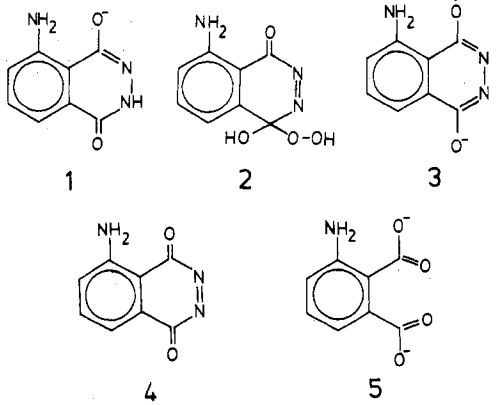
The kinetics of the redox reaction of one-electron-oxidized luminol with molecular oxygen has been studied with chemiluminescent techniques. The rate constants of the forward and reverse reactions have been determined to be 550 ± 100 and (2.5 ± 1.6) × 10^9 M^{-1} s^{-1}, respectively. These values afforded the one-electron-reduction potential of 5-aminophthalazine-1,4-dione with E° = 240 ± 20 mV vs. NHE.

Luminol (**1**) is known to elicit chemiluminescence under almost



1 **2** **3** **4** **5**

an unlimited variety of conditions.[1] It has been shown that in aqueous solutions intense chemiluminescence requires the rapid formation of a short-lived intermediate hydroperoxide (**2**).[2,3,4] Both the recombination of the luminol radical (**3**) with superoxide (reaction 1) and the stoichiometrically equivalent reaction 2 between 5-aminophthalazine-1,4-dione (**4**) with HO_2^- yield **2** in a single step.[4] The monodissociated hydroperoxide (**2**) decomposes quantitatively into N_2 and 3-aminophthalate (**5**).[4] Part of the latter is excited and fluoresces, the chemiluminescence quantum yield being ≈0.012.[3] In previous investigations we were never able to observe directly any reaction between the luminol radical (**3**) and molecular oxygen.[4] Nevertheless, there are a number of papers in the literature[1,5,6] where the weak chemiluminescence reported only makes sense if some molecular oxygen can be presumed to be reduced to $O_2^{-}\cdot$ by the luminol radical (**3**). In analogy with amply documented semiquinone/quinone systems,[7,8] the reaction between O_2 and **3** ought to be written as a redox equilibrium (eq I). Equilibrium I can never be attained due to

$$3 + O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 4 + O_2^{-}\cdot \qquad \text{(I)}$$

the rapid hydrolysis of **4** (reaction 3)[9] and the consumption of **3** through reactions 1 and 4. However, by monitoring the light emitted through reaction 1, it should be possible to determine the

$$3 + O_2^{-}\cdot \xrightarrow{H_2O} 2 \qquad (1)$$

$$4 + HO_2^- \xrightarrow{H_2O} 2 \qquad (2)$$

$$4 + OH^- \rightarrow \text{products} \qquad (3)$$

$$3 + 3 \rightarrow 4 + 1 \qquad (4)$$

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TABLE I: Pertinent Rate Constants (k)

reacn	k, M^{-1} s^{-1}	ref
1	$(2.3 \pm 0.3) \times 10^8$	this work
2	$(5 \pm 2) \times 10^7$	3
3	$(4 \pm 1) \times 10^6$	9
4	$(5.0 \pm 0.5) \times 10^8$	4
5	2×10^{10}	20
7	1.9×10^{10}	21
8	8.7×10^9	21
9	3.65×10^8	22
10	3.6×10^7	22
11	$(9 \pm 2) \times 10^8$	this work

individual rate constants in eq I.

Determination of k_f of the Forward Reaction. On the basis of the experimental accuracy in our previous studies, k_f can be presumed to be less than 10^3 M^{-1} s^{-1}. Since the recombination of the luminol radical (**3**) through reaction 4 competes with the oxygen reaction (eq I), the effect of O_2 can best be studied when

$$2k_4[\mathbf{3}] < k_f[O_2]$$

i.e., [**3**] should be less than 10^{-9} M. At such low concentration of **3** and $O_2^{-}\cdot$ the hydrolysis (reaction 3) of species **4** is quantitative, and thus the reverse reaction in eq I is completely suppressed. The determination of k_f rests on the measurement of the chemiluminescent light emitted by a steady-state radiolyzed aqueous solution containing 10^{-4} M luminol and 0.1 M CO_3^{2-} at pH 10.6 which was purged with N_2O/O_2 mixtures of various composition. ^{35}S in the form of sulfate dissolved in the solution was used as an internal source of radiation. ^{35}S was chosen, as the energy of its β decay is below the Cherenkov threshold. Under these conditions all light originated from luminol chemiluminescence, as was confirmed spectrally. Two different specific activities of ^{35}S were used: 3.04 and 1.52 Ci/dm^3. Setting $G = 6$ (G is molecular events per 100 eV of absorbed energy) for the total radical production, these activities result in the radical production rates of 6.3×10^{-10} and 3.15×10^{-10} M s^{-1}, respectively. Upon radiolysis of an aqueous solution, the primary species OH·, e_{aq}^-, and H· are formed with the following G values: $G_{OH\cdot} = 2.7$, $G_{e_{aq}^-} = 2.7$, and $G_{H\cdot} = 0.6$.[10] These three radicals initiate reactions 5–11 Thus,

$$H\cdot + O_2 \rightarrow HO_2\cdot \quad (5)$$

$$HO_2\cdot \rightleftarrows H^+\cdot + O_2^-\cdot \qquad pK_a = 4.8 \quad (6)$$

$$e_{aq}^- + O_2 \rightarrow O_2^-\cdot \quad (7)$$

$$e_{aq}^- + N_2O \xrightarrow{H_2O} OH\cdot + OH^- + N_2 \quad (8)$$

$$OH\cdot + CO_3^{2-} \rightarrow CO_3^-\cdot + OH^- \quad (9)$$

$$OH\cdot + HCO_3^- \rightarrow CO_3^-\cdot + H_2O \quad (10)$$

$$CO_3^-\cdot + \mathbf{1} \rightarrow \mathbf{3} + CO_3^{2-} + H^+ \quad (11)$$

all primary radicals are transformed into $O_2^-\cdot$ and **3**. The ratio between [$O_2^-\cdot$] and [**3**] is governed by the [O_2] to [N_2O] ratio through the competing reactions 7 and 8. The rate constants for reactions 1–11 are summarized in Table I. The experiments were carried out at 25 °C where the solubility of O_2 and N_2O in water are 1.3×10^{-3} and 2.4×10^{-2} M, respectively.

The light yield was calibrated against the persulfate luminol system[11] and $(3 \pm 1) \times 10^{-3}$ photons per species **3** were detected in the oxygen-saturated system. Within a factor of 2 this photon yield is equal to the one measured upon pulse radiolysis of an identical solution. In the latter case the initial radical concentration is around 10^{-5} M. It is thus seen that irrespective of the radical concentration the chemiluminescent efficiency remains the same.

The steady-state light level is proportional to the rate of the chemiluminescent reaction 1; i.e., the intensity is proportional to the steady-state concentration of both **3** and $O_2^-\cdot$. The results are depicted in Figure 1. The most striking feature of the graphs is the steep rise (>100%) in intensity when the O_2 concentration increases from ~5 to ~30%.

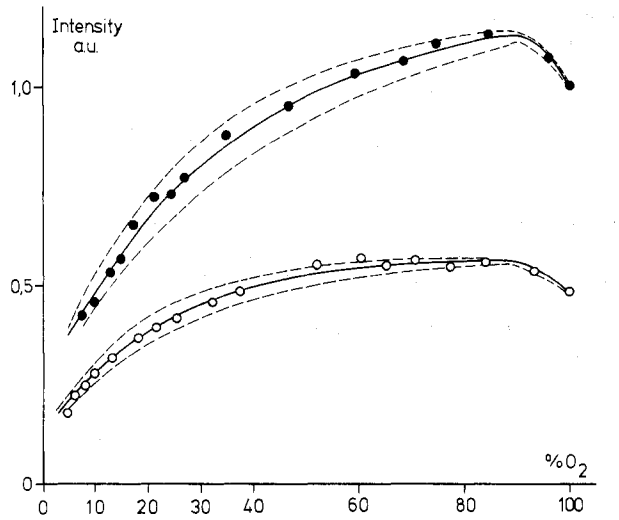

Figure 1. Chemiluminescent intensity as a function of the percentage of O_2 in the N_2O/O_2 purging gas (conditions: 10^{-4} M luminol; 0.1 M CO_3^{2-}; pH 10.6): ●, activity of ^{35}S 3.04 Ci/dm^3; ○, activity of ^{35}S 1.52 Ci/dm^3; full lines calculated for $k_f = 550$ M^{-1} s^{-1}; upper broken lines calculated for $k_f = 650$ M^{-1} s^{-1}; lower broken lines calculated for $k_f = 450$ M^{-1} s^{-1}.

The primary yield of $O_2^-\cdot$ through reactions 5 and 7 increases by no more than 25% in this region ($G(O_2^-\cdot) = 0.6$ and 0.72 at 5% and 30% O_2, respectively). The major increase in $O_2^-\cdot$ through reaction 7 occurs at >50% O_2, a region where the light intensity is almost constant. Thus, the experimental points cannot be accounted for by the primary yields of $O_2^-\cdot$ and **3** undergoing reactions 1 and 4. An additional reaction is required in which further $O_2^-\cdot$ is produced. This is precisely what happens in the forward reaction of eq I. Steady-state treatment of reactions 1 and 4, the forward reaction of eq I, and reaction 12 yielded a

$$2O_2^-\cdot \xrightarrow[CO_3^{2-}]{H_2O} O_2 + H_2O_2 \quad (12)$$

system of equations. The rate of reaction 1 was calculated numerically for various values of k_f by use of the rate constants in Table I, the production rates of the radicals and the primary yields as a function of the O_2 concentration. By means of photon-counting techniques,[12] the rate constant of reaction 12 has been determined to be $(1 \pm 0.5) \times 10^6$ M^{-1} s^{-1} in these solutions. It should be mentioned that the calculations were not sensitive toward k_{12} as long as the latter was put in the range $10^5 < k_{12} < 10^7$ M^{-1} s^{-1}.

The best fit to the experimental points was obtained at $k_f = 550$ M^{-1} s^{-1}. The sensitivity of the light profile toward k_f is demonstrated by the curves calculated with $k_f = 650$ and 450 M^{-1} s^{-1} in Figure 1. Thus, we believe that the error in k_f is less than 20%. By use of this rate constant and the above set of reactions, we were able to simulate quantitatively the oxygen dependence of electrochemically generated luminol chemiluminescence as reported by Kuwana et al.[13] Homogeneous conditions were assumed in this simulation, which appears to be reasonable judging from the experimental description of the above authors.

Determination of the Rate Constant k_r for the Reverse Reaction. The diazaquinone **4** can be rapidly generated through the reaction between luminol (**1**) and ClO_2. Around pH 7 the lifetime

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(12) In the presence of luminol the second-order dismutation of $O_2^-\cdot$ in CO_3^{2-}-containing solutions gives rise to weak chemiluminescence, due to a minor side reaction of $O_2^-\cdot$ with luminol. In a stopped-flow arrangement the light emission, as detected by means of photon counting, probes the major reaction, i.e. the second-order dismutation of $O_2^-\cdot$ (to be submitted for publication).

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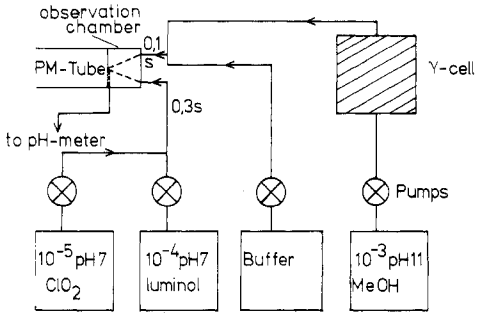

Figure 2. Schematic presentation of the experimental setup utilized for the determination of k_r.

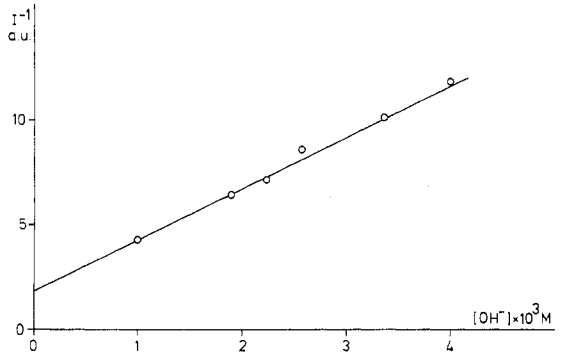

Figure 3. The inverse of the chemiluminescent intensity plotted against $[OH^-]$ as determined by the setup in Figure 2 (condition: 9.7×10^{-7} M $O_2^{-}\cdot$).

of **4** in water is about 1 s. An aqueous solution of $O_2^{-}\cdot$ can be prepared by radiolyzing an air-saturated solution containing 10^{-3} M methanol at pH 11.[14] In such a solution the lifetime of $O_2^{-}\cdot$ exceeds 10 s. The experiments were carried out according to Figure 2. In a continuous-flow system neutral solutions of luminol (10^{-4} M) and ClO_2 (2.5×10^{-6} M) were pumped together. After a delay of 0.3 s, to ensure the quantitative formation of **4**, the outgoing stream was mixed with a superoxide-containing stream and adjusted to the desired pH by introducing a buffer 0.1 s prior to the final mixing. The final mixing occurred in the observation chamber in front of the PM tube. By varying the residence time in the γ cell, we could alter the $O_2^{-}\cdot$ concentration. The latter was determined by pumping the stream into an aqueous solution saturated with $C(NO_2)_4$ and measuring the resulting absorbance of the nitroform anion at 350 nm.[15] In the present experiment there is a competition for **4** between OH^- and $O_2^{-}\cdot$ (reaction 3 and the reverse reaction of eq I). Since $O_2^{-}\cdot$ is always in excess of species **4** (the concentration of **4** in the observation chamber is less than 2×10^{-7} M), the formation of **3** through eq I is followed by reaction 1 yielding light. Taking into account the above competition, the following expression for the light yield L is obtained, where L_0 is the maximum light obtainable.

$$L = L_0 \frac{k_r[O_2^{-}\cdot][4]}{k_r[O_2^{-}\cdot][4] + k_3[OH^-][4]}$$

We have performed three similar sets of experiments at three different $O_2^{-}\cdot$ concentrations. In each one the pH was varied. A typical experiment is depicted in Figure 3. As can be seeen from the figure, the light yield diminishes at constant $O_2^{-}\cdot$ concentration as the pH is raised. It should be mentioned that due to the high reaction rates involved, light emission occurs under inhomogeneous conditions. However, since the primary competition reactions are of pseudo first order, the actual light measured is always proportional to the total light that one would obtain under homogeneous conditions. The proportionality constant is determined by the flow characteristics of the system, which is the same in all experiments. In the same experimental setup, the light yield measured upon mixing alkaline H_2O_2 (10^{-2} M) with a stream of **4** (reaction 2) is roughly equal to the value obtained from the intercept in Figure 3. Recalling from a previous study that reactions 2 and 3 have the same chemiluminescent efficiency,[4] the above observation proves the internal consistency in the present measurements.

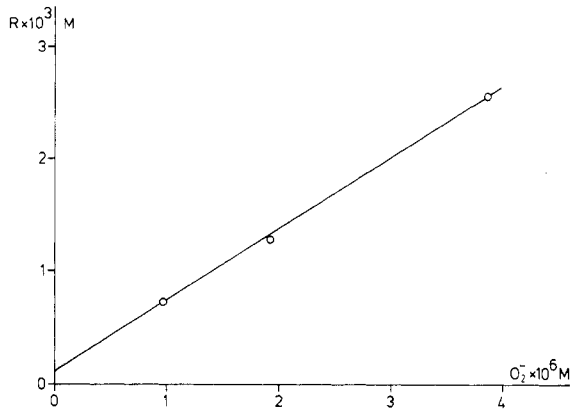

Figure 4. The intercept/slope ratio $R = (k_r/k_3)[O_2^{-}]$ obtained from Figure 3 and similar experiments plotted vs. $[O_2^{-}\cdot]$.

By dividing the intercept of the straight line obtained in any particular experiment by its slope, we can calculate the ratio

$$R = k_r[O_2^{-}\cdot]/k_3$$

From Figure 4 where R is plotted against $[O_2^{-}\cdot]$, $k_r/k_3 = 625 \pm 60$ is determined. Finally, employing the reported value of $k_3 = (4 \pm 1) \times 10^6$ M^{-1} s^{-1}, we calculate k_r to be $(2.5 \pm 1.6) \times 10^9$ M^{-1} s^{-1}. The sources of error in k_r are as follows: 10% in the spread of the straight line in Figure 3, 25% in the determination of $[O_2^{-}\cdot]$, 5% in the determination of $[OH^-]$, and 25% in the determination of k_3. In the above-reported experiments we observed a weak background chemiluminescence generated through reaction 3. Since the magnitude of this background was more than 100 times lower than L_0, it did not interfere with the measurement of k_r. The mechanism of the weak chemiluminescence resulting from reaction 3 has been studied in some detail in ref 16.

The Redox Potential of 5-Aminophthalazine-1,4-dione (4). Combining k_f and k_r, we calculate the equilibrium constant K_1 of eq I to be 2.2×10^{-7}. Let us estimate the error in this constant. As was shown above, the uncertainty in k_f and k_r are 20% and 65%, respectively. In summary, the total error in K_1 amounts to less than 85%; thus

$$K_1 = (2.2 \pm 1.9) \times 10^{-7}$$

From the above equilibrium constant K_1 and the known redox potential of the $O_2/O_2^{-}\cdot$ couple (−0.155 V),[17] the redox potential $E°$ for the process

$$4 + e^- \rightarrow 3$$

is calculated to be $+0.24 \pm 0.02$ V vs. NHE. Since this redox potential is the first one ever reported for a diazaquinone, it is interesting to compare it to values obtained for typical quinones. A scrutiny of the $E°$ values compiled in ref 7 indicates that the redox potentials of diazaquinones are more positive by at least 300 mV than those pertaining to an isoelectronic quinone analogue. It is therefore not surprising that the rate constant k_r is close to the diffusion-controlled limit. Since the redox potentials of other phthalazine-1,4-diones with less electron-donating substituents

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will surely have more positive $E°$ values than +240 mV, the k_r values for these should also lie in the diffusion-controlled limit. Consequently, it is expected that log k_f for the reaction of diazasemiquinones with O_2 will be proportional to the $E°$ value of the corresponding diazaquinone. Applying the Marcus equation[18]

$$\Delta G^{\ddagger} = \frac{\lambda_0}{4}\left(1 + \frac{\Delta G°}{\lambda_0}\right)^2$$

to k_r and k_f in eq I, we obtain a λ_0 value of 24 kcal/mol. This compares very favorably to $\lambda_0 = 18 \pm 2$ kcal/mol as determined for a series of quinones.[7] The present λ_0 value is compatible with that of an electron transfer without any significant change of bonds if the mean radii of the solvated species are assumed to be about 4 Å. All in all, the reaction examined in this work appears to be fully consistent with an electron-transfer process.

Previously, the rate constant for reaction 2 was determined[3] to be $(5 \pm 2) \times 10^7$ M^{-1} s^{-1}. Yield measurements indicated that this reaction could involve an electron transfer.[4] Applying the Marcus equation to reaction 2 and utilizing +0.200 V as the $E°$ value of the $O_2^{-}\cdot/HO_2^{-}$ couple,[19] we predict the rate constant k_2 to be 10^7 M^{-1} s^{-1}. Thus, we conclude that the rate-determining step of reaction 2 may very well be an electron transfer.

Registry No. **1**, 521-31-3; **3**, 89596-65-6; **4**, 60851-83-4; **5**, 27846-29-3; $O_2^{-}\cdot$, 11062-77-4; O_2, 7782-44-7; $CO_3^{-}\cdot$, 16518-46-0.

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Infrared Matrix Isolation Study of the 1:1 Molecular Complexes of the Hydrogen Halides and Hydrogen Cyanide with Cyclopropane

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The matrix isolation technique has been used to isolate and characterize the 1:1 hydrogen-bonded complexes between the hydrogen halides (from HF to HI) and hydrogen cyanide and cyclopropane, c-C_3H_6. In each case, a perturbed vibrational mode of the complexed acid was observed, shifted 10–200 cm^{-1} to lower energies from the position of the corresponding "free" acid. The magnitude of the shift correlated directly with the strength of interaction and dipole moment of the acid but not with the proton affinity of the halide anion. Several perturbed modes of the cyclopropane subunit in the complex were observed, and again the magnitude of shift correlated with strength of interaction. For the two most strongly bound complexes, HF·c-C_3H_6 and HCl·c-C_3H_6, the low-frequency bending mode was identified as well, near 400 cm^{-1}. The spectra are consistent with the gas-phase structure from rotational spectroscopy, in which the hydrogen of the hydrogen halide is bonded to the midpoint of one carbon–carbon bond, and the hydrogen halide lies in the plane of the three-membered carbon ring. In addition, evidence was obtained for the existence of a 2:1 complex 2HX·c-C_3H_6, but no structural determination could be made.

Introduction

Cyclopropane, c-C_3H_6, has been known for years to exhibit unusual chemical properties due to the high degree of strain in its three-membered ring.[1] These properties are olefinic in nature, and various models proposed for the bonding in c-C_3H_6 all suggest that substantial electron density resides outside of the line connecting the carbon nuclei (i.e., a bent bond).[2,3] Theoretical[4] and experimental[5] measurements confirm, in a general sense, these predictions and suggest that protonation might well occur in these regions of high electron density. Stimson[6,7] and others have shown that the isomerization of cyclopropane to propylene in the gas phase is catalyzed by both Lewis acids and Brønsted acids, such as the hydrogen halides. In particular, he found that the activation barrier was lowered by roughly 25 kcal/mol by the addition of HBr in catalytic amounts and that addition of BBr_3 increased the rate by an additional factor of 10. He was led to invoke a weakly bound gas-phase complex, in contrast to the protonated complex which has been invoked to explain the solution-phase chemistry of c-C_3H_6. The gas-phase proton affinity of cyclopropane[8] has been measured to be 179 kcal/mol, which while very high for a hydrocarbon is still not sufficient to remove a proton from any of the hydrogen halides. Rather, a hydrogen-bonded complex seems reasonable for the interaction leading to the gas-phase catalytically induced isomerization; hydrogen bonding has been postulated as being responsible for the anesthetic action of cyclopropane.[9]

Rotational spectroscopy of weakly bound complexes formed through free-jet expansions and supersonic nozzles has provided structural information on a number of hydrogen-bonded com-

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