

mole of detergent corresponds to an increase of 11.5% in the intermicelle distances and this is evidently significant enough to reduce the intermicelle forces responsible for transmitting the helical order to the macroscopic scale. At this present time the definitive experiments on the precise shape of the micelle in the cholesteric systems has not been made, but also the complex forces between micelles with electrical double layers separated at distances comparable with the Gouy layer still represents a serious challenge to the model.

The results for different optically active guests at a single concentration in a cholesteric phase of low twist are useful because they indicate the relative sign of the effect on twist, some decrease the pitch length, some have very little effect, and some increase the pitch. Even though the relative concentration of optically active guest is small the pitch ranges over a factor of 5. The result for the opposite enantiomers of 2-octanol is unexpected. This is a compound with a single optical center and is located with the OH group at the interface of the micelle and the chiral center attached. Both enantiomers *increase* the pitch by an equal amount. On the pairwise interaction theory⁹ they would be expected to have equal and opposite effects. The experimental result suggests that they are, in both optical forms, a contributor to a decrease in helicity of the micelle planes.

The effect, on the pitch length, at all values of ($2X_L - 1$) for the LAK (Figure 3), of the two guests that decrease the pitch, show that it is possible to have a guest which is more effective in increasing the twist of a host phase at low twists than at high, but the effect is very small and for the second guest absent. Experiments show that the pitch lengths are near an order of magnitude longer than needed for reflection bands in the visible range and that optically active guests do not decrease the pitch by large amounts making it unlikely that mesophases of this type can ever be made with a visible reflection band. This is contrary to a prior opinion⁹ that twisting power in lyotropic cholesterics are similar to those in thermotropics and that color reflection will be found in such systems.

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Registry No. LAK, 76402-41-0; LSK, 83666-40-4; LVK, 83666-41-5; gardol, 137-16-6; colchicine, 64-86-8; progesterone, 57-83-0; *l*-2-octanol, 6169-06-8; *d*-2-octanol, 5978-70-1; cholesterol, 57-88-5; ergosterol, 57-87-4; brucine, 357-57-3; yohimbine, 146-48-5; cinchonidine, 485-71-2.

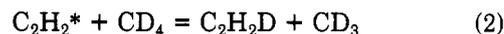
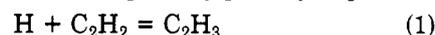
COMMENTS

Equivalence of Vinylidene and $C_2H_2^*$: Calculated Rate Constant for Vinylidene Abstraction from CH_4

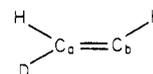
Sir: A long-lived excited state of acetylene, denoted by $C_2H_2^*$, often has been invoked as the major intermediate species in the photolysis of C_2H_2 .¹ The structure of the intermediate remains obscure. Recently, Laufer, on the basis of spectroscopic evidence, has suggested that triplet vinylidene radicals (3B_2 , $H_2C=C$) are a possible intermediate in the vacuum ultraviolet flash photolysis of acetylene as well as the combination of two triplet CH_2 radicals.² In the latter, the isotopic distribution of product acetylene supports the assignment to vinylidene.³ There is no compelling evidence, however, to equate the $C_2H_2^*$ intermediate suggested in low-intensity photolysis experiments with vinylidene. The ground state of the vinylidene radical is a singlet (1A_1) with a very short lifetime calculated to be 10^{-11} s.⁴ Experimental evidence indicates a lifetime toward rearrangement to C_2H_2 of 10^{-10} s⁵ which make it highly unlikely that (1A_1) $H_2C=C$ will be involved in chemical processes. Alternatively, triplet (3B_2) vinylidene, which lies 42 ± 3 kcal/mol above the singlet,^{4,6} must overcome an activation energy barrier of about 50 kcal/

mol⁷ which is suggestive of a long lifetime thereby increasing its susceptibility to chemical reaction. In a study of the 1470-Å acetylene-photosensitized decomposition of CH_4 , Takita et al.⁸ examined the isotopic distribution of the ethylene produced in the $C_2H_2-CD_4$ and $C_2D_2-CH_4$ systems. In the former, the ethylenes were either d_0 or d_1 ; in the latter either d_3 or d_4 . Notable was the absence of product ethylene- d_2 in either mixture. As will be shown these results offer convincing evidence that the structure of $C_2H_2^*$ is identical with $H_2C=C$, probably in the 3B_2 state.

The source of ethylene (including the various deuterated species) in the Takita⁸ study was the disproportionation of vinyl radicals. the source of vinyl was by reaction 1 or 2, the H being formed in the primary photolytic process.



If we consider reaction 2 in detail and assume the structure of $C_2H_2^*$ resembles $H-C\equiv C-H$, then the vinyl radical produced in (2) will have the structure



On the basis of bond strength considerations, it is expected that either the H or D on C_a will be transferred to the conjugate vinyl radical in the disproportionation pro-

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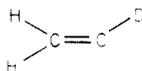
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cess. In the case of the H atom on C_a the dissociation energy of the H-C bond is 37.3 kcal/mol determined from $\Delta H_{f,298}(C_2H_3)$,⁹ $\Delta H_{f,298}(C_2H_2)$,¹⁰ and $\Delta H_{f,298}(H)$ ¹⁰ = 69.0, 54.2, and 52.1 kcal/mol, respectively. The C_b -H bond is significantly stronger, 83 kcal/mol, based upon $\Delta H_f(H_2C=C)$ (1A_1) of 100 kcal/mol.⁶ While a small isotope effect may be expected, there is a high probability that the D atom will be transferred resulting in a ethylene- d_2 , a result in conflict with experiment.

If, however, the structure of $C_2H_2^*$ is that of a vinylidene species $H_2C=C$, then the vinyl radical produced in (2) can only be



As before, an H atom is expected to be transferred resulting in either ethylene- d_0 or - d depending only upon the level of deuteration of the recipient radical. It is clear that no ethylene- d_2 can be produced if the precursor is vinylidene.

The mechanism is predicated upon the absence of a 1,2 hydrogen migration in the vinyl radical prior to the disproportionation process. The result of a migration would place the D atom on the same C atom as an H which is indistinguishable from the vinyl radical produced from the $H-C\equiv C-H$ structure. The potential barrier to a 1,2 hydrogen migration in vinyl radicals has been calculated to be 57 kcal/mol¹¹ so the initially formed vinyl is stable with respect to isomerization.

Takita et al.⁸ note that hydrogen abstraction from CH_4 by C_2H_3 is unimportant in their system. The modified mechanism suggested above requires that $H_2C=C$ abstract from CH_4 . There are no rate constants in the literature to substantiate either position. Since the required reaction is a simple hydrogen-abstraction process we have obtained estimates of both the preexponential and activation energies of the reactions by semiempirical methods such as the BEBO (bond energy-bond order)¹² or BSBL (bond strength-bond length)¹³ techniques.

A detailed discussion and computer code of the BEBO calculation has been published elsewhere¹⁴ and differences between the activation energy results of the two methods described.¹³ It is recognized that the Arrhenius frequency factor obtained from the BEBO calculation is as accurate as that obtained from BSBL. The preexponential obtained from the BEBO calculation for both the $H_2C=C$ and C_2H_3 abstraction from CH_4 were equal, i.e., 5×10^{-13} cm³ molecule⁻¹ s⁻¹. The value appears reasonable and comparable to the preexponential for H atom abstraction from CH_4 by CH_3 .¹⁵

The input data required for the BSBL calculation of the H-atom abstraction reaction by C_2H_3 are listed in Table I. The E_a is calculated to be 8.7 kcal/mol which in conjunction with the previously determined frequency factor yields an estimated value for $k_{(C_2H_3+CH_4)} \approx 2 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

TABLE I

bond type (x-y)	R_{xy} , ^a Å	V_{xy} , ^b kcal/mol	W_{xy} , ^c cm ⁻¹	EA, ^d eV	
				x	y
H-CH ₃	1.094 ^e	107.3	2916 ^e	0.75	0.08
H-C ₂ H ₃	1.086 ^f	112.8	3020	0.75	1.4 ^h
H ₃ C-C ₂ H ₃	1.488 ^e	98.7	950	0.08	1.4
H-HC ₂	1.083 ⁱ	120.4	3250 ⁱ	0.75	3.73
H ₃ C-CCH ₂	1.488	119.4 ^j	1100	0.08	1.79 ^{h,j}

^a Bond length. ^b Bond energy. Sum of the bond strength based upon heats of formation and the zero-point energy of the stretching vibration. Data from ref 6, 9, 10; J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, *Nat. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969). ^c Stretching frequency. ^d Electron affinities. ^e G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, NJ, 1967. ^f Reference 13. ^g Based upon H-C₂H₃ in ref e. ^h W. Lindinger, D. L. Albritton, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.*, 63, 3238 (1975); J. Chandrasekhar, R. A. Kahn, and P. v. R. Schleyer, *Chem. Phys. Lett.*, 85, 493 (1982). ⁱ Y. Osamura and H. F. Schaeffer III, *Chem. Phys. Lett.*, 79, 412 (1981). ^j See discussion.

The input data for the vinylidene abstraction reaction from CH_4 also are listed in Table I. It is highly unlikely that (1A_1) $H_2C=C$ will abstract from CH_4 because of its short lifetime plus the endothermicity of the reaction (20 kcal/mol). The long-lived triplet (3B_2), however, may abstract. The BSBL method utilizes a bond energy which is essentially independent of electronic state and the role of the excitation energy is not considered in the model. The reaction products, arising from either singlet or triplet vinylidene are the same, i.e., two doublets, which adiabatically correlate with both singlet or triplet reactants. Since the individual transition states from either singlet or triplet vinylidene are structurally quite similar and probably energetically separated by only a few kcal/mol, the reverse activation energies are comparable and the overall reaction thermochemistry completely defined. Triplet $H_2C=C$ has uncoupled electrons which present an open shell to facilitate bonding as compared to the paired electrons of the singlet. The difference in ΔH_f represents, in part, the energy required to unpair the electrons. Since the path from reactant to transition state will involve the initial reactant energy, the value for the "bond energy" shown in Table I and used in the calculations has been modified to include the energy associated with the triplet. The E_a 's calculated by the BSBL method are quite sensitive to the bond energy values. Depending upon the value for the 1A_1 - 3B_2 separation chosen, the E_a varies but is best expressed as 5.5 ± 0.5 kcal/mol which leads to $k_{(H_2C=C+CH_4)} \approx 5 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ or 230 times faster than $k_{(C_2H_3+CH_4)}$.

In summary, the isotopic distribution of ethylene produced in the 1470-Å photolysis of both C_2H_2 - CD_4 or C_2D_2 - CH_4 mixtures observed by Takita et al.⁸ provide evidence that $C_2H_2^*$ is best represented structurally by vinylidene, $H_2C=C$, probably in the 3B_2 state. The differences in reactivity between C_2H_3 and $H_2C=C$ probably arise from activation energy considerations. The results of this work may affect other systems, for example, photochemistry and kinetics in the stratospheres of the Jovian planets and Titan. If the primary fate of $C_2H_2^*$ in these atmospheres is abstraction of hydrogen from CH_4 , then this represents the dominant pathway for dissociating CH_4 .^{1,16} However, before this possibility can be assessed, appro-

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ropriate experiments must be performed to investigate the relative reactivity of the vinylidene radical toward H₂, alkanes, alkenes, alkynes, and other hydrocarbon radicals.

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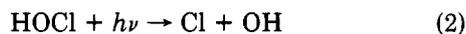
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Upper Limit for the Atomic Oxygen Yield in the 308-nm Photolysis of HOCl

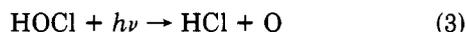
Sir: The possibility that HOCl might serve as an inert chlorine reservoir in the stratosphere has been ruled out by the absorption cross-section measurements of Molina and Molina¹ and of Knauth, Alberti, and Clausen,² which show significant absorption at wavelengths greater than 300 nm and imply a short (ca. 30 min) photolytic lifetime for HOCl. The results of Knauth et al. provide the currently accepted values of HOCl cross sections between 200 and 420 nm and of the equilibrium constant ($K_1 = 0.082$ at 298K) for the reaction



Molina, Ishiwata, and Molina³ showed that the major photolytic pathway for HOCl at 310 nm is



Their value of $(5.9 \pm 0.6) \times 10^{-20}$ cm² for the cross section for process 2 in the range 307-309 nm, based on an absolute measurement of the OH yield, is in excellent agreement with Knauth et al.'s value of $(6.2 \pm 0.6) \times 10^{-20}$ cm² for the total cross section at 310 nm. However, the alternative, albeit less likely, process



is energetically possible at these wavelengths, and the quoted limits of error (essentially one standard deviation in both cases) could accommodate a value as high as 20% for the fraction of decomposition occurring by process 3. The aim of the present work was to measure, or at least set an upper limit for, the fraction of decomposition by pathway 3. Our method was to use atomic resonance fluorescence to detect any O atoms produced in the 308-nm laser photolysis of HOCl.

Chlorine monoxide (Cl₂O) was prepared by reacting chlorine gas with dry, yellow mercuric oxide, excess chlorine being separated from the product in a LeRoy still. Mixtures of approximately 1 torr of Cl₂O with 16 torr of H₂O were allowed to equilibrate in blackened storage bulbs

for several hours before use. Typically, equilibrium concentrations calculated with $K_1 = 0.082$ were [Cl₂O] ~ 0.85 torr, [HOCl] ~ 0.62 torr, and the ratio of calculated 308 nm absorption by HOCl and Cl₂O was 1/4.85. Gases were handled in an all-pyrex vacuum system with greaseless teflon-key stopcocks. Gas pressures were measured with a Texas Instruments quartz spiral gauge. NO₂, for use as an actinometer, was prepared by reacting Matheson CP nitric oxide with excess O₂, purified by distillation at -78 °C, and mixed with water vapor in the flow system just prior to photolysis.

The photolysis cell consisted of a 25 cm length of 50 mm diameter Pyrex tube having a Suprasil window affixed with Torr-seal epoxy resin at each end. Gas mixtures to be photolyzed were pumped through this tube at pressures near 1 torr. Unfocussed pulses of 308-nm radiation from an XeCl laser (Lumonics model TE861-T) passed along the axis of the tube to a laser power meter (Scientech model 364) at the exit window. The pulse repetition frequency was 70 Hz and the average pulse energy was typically 40 mJ, as measured at the exit window. Four access ports were grouped about the middle of the tube. One pair of opposing ports held a flowing, microwave-powered atomic oxygen resonance lamp and a Woods horn. Of the other pair of ports, at right angles to the first pair, one was blanked off and the other held an Acton 130-N interference filter, and a tubular glass collimator leading to an EMR 541-G solar-blind photomultiplier. Preliminary experiments with oxygen atoms from a microwave discharge in O₂/He mixtures showed that this fluorescence system responded selectively to oxygen atoms provided the argon and oxygen for the lamp were dried over silica gel at -78 °C. At low O-atom concentrations the fluorescence signal varied linearly with atom concentration, both with O from discharged O₂/He mixtures and with O from NO₂ photolysis. To reduce the possibility of observing O atoms due to photolysis by the resonance lamp, the microwave generator for the lamp was modulated at 70 Hz and the laser was triggered close to the leading edge of the lamp output waveform. Sufficient pumping speed was available to remove photolysis products between lamp pulses; in practice, the extent of photolysis proved to be low enough to make this unnecessary.

Signals from the 541-G photomultiplier were amplified (amplifier bandwidth ~ 400 kHz) and taken to an oscilloscope, a PAR Model HR-8 lock-in amplifier tuned to 70 Hz, and a PAR Model TDH-9 100-channel waveform eductor. The output of the lock-in amplifier was proportional to the intensity of scattered 130-nm radiation reaching the photomultiplier. This signal diminished by up to a factor of 10 when gas mixtures were introduced into the cell, mainly because of absorption of the 130-nm radiation by H₂O. For this reason, NO₂ photolysis measurements were made in the presence of excess H₂O, and the results of experiments with NO₂/H₂O and equilibrated Cl₂O/H₂O mixtures were compared at similar levels of the lock-in amplifier signal. Over a small range, fluorescence signals were scaled in inverse proportion to the size of this scattered light signal. The percentage absorption of 308-nm radiation was monitored in a 1-m absorption cell, downstream from the photolysis cell, using a tungsten strip-filament lamp, a 308-nm interference filter, a 1P28 photomultiplier, and a Keithley Model 417 picoammeter.

The waveform eductor was used to monitor a 200-μs section of photomultiplier signal which included the region of the laser flash. With allowance for duty cycle, the effective time constant of the eductor was about 355 s. At a repetition frequency of 70 Hz, this corresponds to a

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