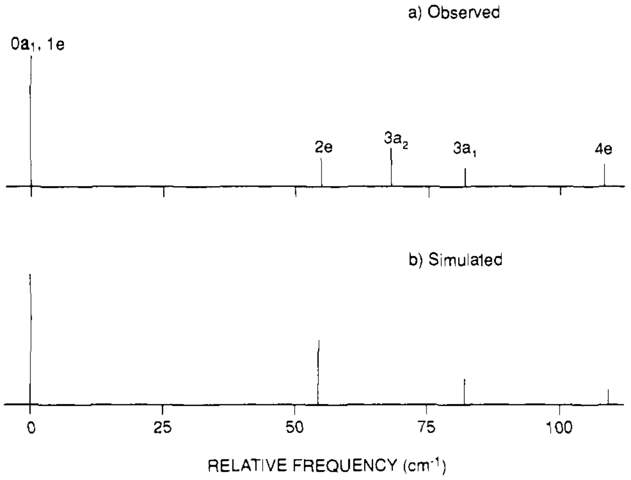

Figure 12. Stick diagram of the (a) observed and (b) simulated excitation spectra of CdMeCp near the Ã–X̃ origin band. Diagram a represents the average of three scans around the Ã–X̃ origin. See text for discussion.

$2p\pi$ in character (see the discussion on the electronic structure of ZnCp and CdCp in ref 15 for more details).

Generally, if there is no shift in the phase angle, θ, between the minima of the ground and excited electronic state torsional potential wells, i.e., there is no change in methyl group conformation, only the $0a_1$–$0a_1$ and 1e–1e transitions will be observed with any significant intensity from Franck–Condon arguments. Presumably, this is the reason why in the B̃–X̃ band system of CaMeCp, transitions to the higher torsional levels are not seen in Figure 5. However, this is not the case for the Ã–X̃ system of CaMeCp, as discussed above. The 2e–1e, $3a_2$–$0a_1$, $3a_1$–$0a_1$, and 4e–1e transitions are all observed, which implies immediately that θ is significantly different from 0 for the Ã–X̃ transition. The actual value for θ can be determined from the relative intensities of the torsional bands. As described by Spangler and Pratt,[47] the Franck–Condon factors (FCFs) for the various torsional transitions can be achieved using the eigenvectors obtained by matrix diagonalization of the torsional Hamiltonian. We have performed such calculations for the appropriate torsional transitions of CaMeCp. The closest agreement between the calculated and experimental intensities of the torsional bands for both the excitation and dispersed fluorescence spectra is obtained when a value of 30° for θ is used. To illustrate this, we show in Figure 12 the calculated and observed excitation spectrum of CaMeCp in stick diagram fashion. The agreement in intensities is clearly quite good with the possible exception of the 2e–1e transition. In the case of the a_1–a_2 transition, its intensity cannot be simulated simply by the Franck–Condon factor (which is 0) since this transition becomes allowed only if overall rotation of the molecule is taken into account.

IV. Conclusion

Laser excitation and dispersed fluorescence spectra of CaCp, CaMeCp, and CaPy have been presented and discussed. These spectra showed extensive vibrational structure which was attributed to excitation of both skeletal and intra-ring modes. From this structure, we were able to confirm that a ring-bonding scheme is adopted by these molecules in the gas phase, as suggested earlier by Bernath and co-workers.[8,9] The electronic spectra of d_5-CaCp and d_4-CaPy were employed to assist in the assignment of intra-ring vibrations of CaCp and CaPy. Strong evidence of single quantum excitation of two of the six e_2 modes of CaCp was observed which indicates that this molecule is Jahn–Teller active in its $\tilde{A}^2E_1$ electronic state.

In the case of CaMeCp, very low-frequency, irregularly spaced bands were attributed to hindered rotation of the methyl group. From this structure, the barriers to methyl free rotation in the X̃ and Ã electronic states of CaMeCp were determined as well as the change in conformation of the methyl group on Ã–X̃ excitation.

Acknowledgment. We would like to thank the National Science Foundation for support of this work via Grant No. CHE-9005963. A.M.E. gratefully acknowledges the award of a NATO/SERC and Ohio State postdoctoral fellowships during his stay at The Ohio State University. E.S.J.R. greatly appreciates the award of a 1991 Rohm and Haas and a 1992 Phillips Petroleum fellowships.

Photochemistry of Matrix-Isolated Diazoethane and Methyldiazirine: Ethylidene Trapping?

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Received March 24, 1992

Abstract: Photolysis of matrix-isolated diazoethane (**1a**) at 8 K produces mainly ethene (**4a**), along with a small amount of 3-methyldiazirine (**2a**). ESR experiments employing a variety of irradiation conditions and matrix media (Ar, N_2, Xe) show that triplet ethylidene (**3T**) is not an observable photoproduct. Similar experiments fail to reveal direct evidence for either singlet or triplet ethylidene by IR or UV–vis spectroscopy. Photolysis of nascent 3-methyldiazirine (**2a**) also fails to yield ethylidene. Deuterium substitution produces no detectable change in the chemistry. In carbon monoxide-doped matrices, photolysis of **1** generates 3-methyldiazirine (**2**) and ethene (**4**) as well as a small amount of methylketene (**5**). The most plausible interpretation of these results postulates that (i) trapping of incipient singlet ethylidene (**3S**) by CO competes with the facile hydrogen migration and (ii) intersystem crossing to the triplet does not compete with hydrogen migration.

Carbenes frequently rearrange via intramolecular 1,2-hydrogen migrations to form alkenes. Both theoreticians and experimentalists have expended considerable effort investigating these facile rearrangements.[2,3] Ethylidene (**3**, methylcarbene) holds special

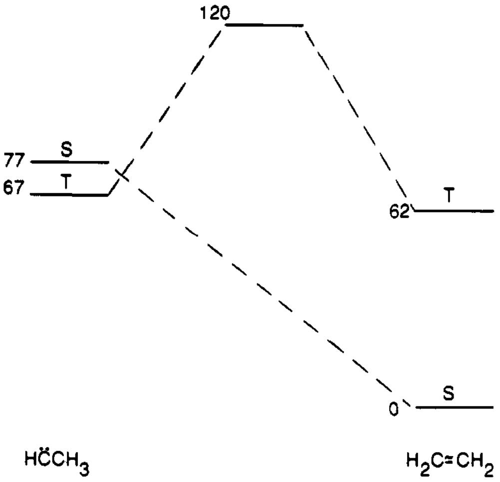
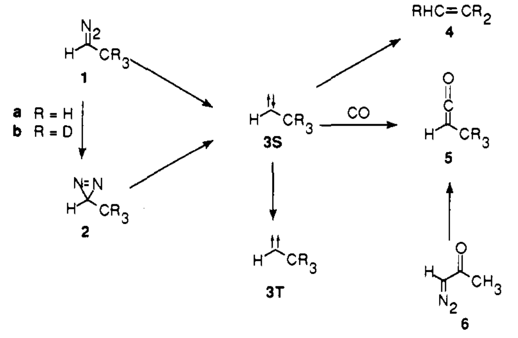
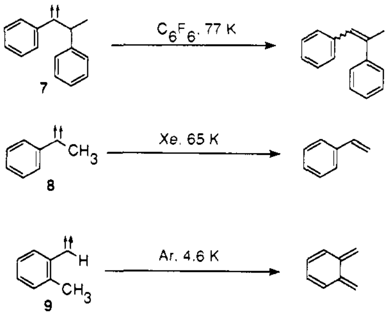


Figure 1. Diagram of the calculated relative energies of singlet (S) and triplet (T) C_2H_4 species (kcal/mol).[8d]

Scheme I



Scheme II



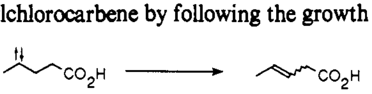
importance, as it is the simplest carbene which can undergo a 1,2-hydrogen migration.[4] Theoretical investigations of 1,2-shifts in carbenes focus on ethylidene (**3**), precisely because it is the archetypal example. In contrast, experimental investigations of 1,2-shifts in carbenes generally avoid ethylidene (**3**) because of the difficulty of safely handling ethylidene precursors, such as diazoethane (**1**) and 3-methyldiazirine (**2**). The chemistry of free ethylidene is also of interest for the purpose of comparing its reactivity with that of metal-bound ethylidene. The involvement of surface-bound ethylidene as a key intermediate in the mechanism of alkene hydrogenation at catalytic metal surfaces is currently controversial.[5] Terminal[6] and bridging[6,7] ethylidene complexes are ubiquitous in organometallic chemistry. In this article, we describe our efforts to generate and characterize ethylidene (**3**) upon photolysis of matrix-isolated diazoethane (**1**) and 3-methyldiazirine (**2**) (Scheme I).

Calculations predict that triplet ethylidene lies below singlet ethylidene in energy, with values for the T_0–S_1 gap of 3–10.7 kcal/mol.[8] Pople et al. recognized that their level of theory favored triplets and as a result proposed a best estimate for the T_0–S_1 splitting of 3–4 kcal/mol, based on the known T_0–S_1 gap of methylene and calculations of the reaction energy of the isodesmic process:[8d]

$$CH_3CH\ (\text{singlet}) + CH_2\ (\text{triplet}) \rightarrow CH_3CH\ (\text{triplet}) + CH_2\ (\text{singlet})$$

Calculations predict large barriers (~50 kcal/mol) for 1,2-hydrogen migration on the triplet surface.[8d,9] Calculations disagree on whether singlet ethylidene is a minimum on the energy surface and on the magnitude of the barrier to 1,2-hydrogen migration. Figure 1 presents a simple diagram of the calculated energies of the various C_2H_4 species.[8d] Early calculations reported large activation barriers (≥20 kcal/mol) for 1,2-hydrogen shift in singlet ethylidene;[10] however, as higher levels of theory were developed, the calculated values decreased dramatically to 3 kcal/mol or less.[8d,11] In fact, Raghavachari et al. concluded that singlet ethylidene is not a minimum on the potential energy surface but is the transition state for scrambling of hydrogens in ethene.[11b] The highest level calculation to date (MP4SDTQ/6-311G**//MP2/6-31G*+ZPE) yields an energy barrier of 0.6 kcal/mol for the 1,2-hydrogen shift of singlet ethylidene to ethene.[12] Thus, theory indicates that singlet ethylidene will be difficult, if not impossible, to observe directly, but that triplet ethylidene may be relatively long-lived at very low temperatures.

Recent experimental investigations of 1,2-hydrogen migrations focused primarily on singlet ground-state carbenes (i.e. carbenes stabilized by heteroatom substituents). Liu and Bonneau obtained the absolute rate constant ($3.04 \pm 0.05 \times 10^6\ s^{-1}$) for hydrogen shift in methylchlorocarbene by following the growth of its pyridine ylide produced upon laser flash photolysis of methylchlorodiazirine in the presence of varying concentrations of pyridine.[13] Their



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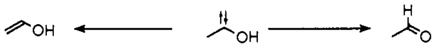
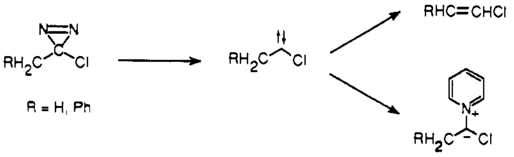
result agrees well with the rate constant (1.4×10^6 s^{-1}) obtained independently from an investigation of the same carbene by photoacoustic calorimetry.[14] Liu et al. also applied the pyridine ylide technique to benzylbromo-,[15a] benzylchloro-,[15b] and (phenoxymethyl)chlorocarbene.[15c] The rate constants for 1,2-hydrogen migration in each of the aforementioned carbenes are on the order of 10^6–10^8 s^{-1} at room temperature, and activation energies range between 3 and 7 kcal/mol. Transient benzylchlorocarbene itself has been observed and its decay monitored by time-resolved absorption spectroscopy.[15b] Calculations predict relatively large barriers for the two possible 1,2-hydrogen migrations in singlet 1-hydroxyethylidene: 28 kcal/mol for the barrier leading to acetaldehyde and 23 kcal/mol for the barrier leading to vinyl alcohol.[16] Theory and experiment currently disagree over which barrier is higher.[16]



Investigations of 1,2-hydrogen migrations in triplet ground-state carbenes (i.e. carbenes not stabilized by heteroatoms) are less numerous. Hydrogen shifts have been observed directly in matrix-isolated carbenes.[2b] (Scheme II). Tomioka et al. monitored the thermal 1,2-hydrogen shift in 1,2-diphenylpropylidene (**7**) utilizing ESR spectroscopy.[17] McMahon and Chapman examined the thermal 1,2-hydrogen shift of triplet 1-phenylethylidene (**8**) in a xenon matrix by IR spectroscopy.[18] In addition, they observed a thermal 1,4-hydrogen migration in triplet *o*-tolylmethylene (**9**) in an argon matrix at 4.6 by IR, UV–vis, and ESR spectroscopy.[18] Stevens et al. provided an indirect estimate for the activation energy (1.1 ± 1 kcal/mol) for the 1,2-hydrogen migration in 1-carboxypent-4-ylidene.[19] Recently, Modarelli and Platz generated the pyridine ylide of dimethylcarbene by laser flash photolysis and determined the lifetime of dimethylcarbene to be between 1 and 100 ns.[20] Adamantanylidene and homocubanylidene have been intercepted by pyridine and detected by laser flash photolysis techniques.[21] The 1,2-hydrogen migration reactions of these carbenes present an interesting case, since the rearrangement can lead only to highly-strained products. At present, no simple monoalkyl-substituted carbenes (R$\ddot{C}$H) have been spectroscopically observed.



Frey[22] and Kibby and Kistiakowsky[23] reported gas-phase photolyses of ethylidene precursors in the 1960s. Irradiation of diazoethane (**1a**) yielded primarily ethene (**4a**) and acetylene, along with minor amounts of 2-butene. In both investigations. the authors postulated that irradiation of diazoethane forms ethylidene, which then either undergoes hydrogen migration to produce vibrationally excited ethene or reacts with another molecule of diazoethane to form 2-butene. In the gas phase, excited ethene fragments to give acetylene and hydrogen. Photolyses of diazoethane (**1a**) in the presence of propene gave products of formal carbene addition (*cis*- and *trans*-dimethylcyclopropane).[22] Irradiation of diazoethane in the presence of O_2 led to the conclusion that about 3% of ethylidene was formed as the triplet.[23] Frey and Stevens also studied the photolysis of 3-methyldiazirine, which gave only ethene and acetylene.[24] They proposed ethylidene as an intermediate, although they did not observe products resulting from formal carbene addition or insertion. Ethylidene has also been proposed as an intermediate in the short wavelength photolysis of propene (147 nm)[25] and 1,1,2-trimethylcyclopropane (185 nm).[26]

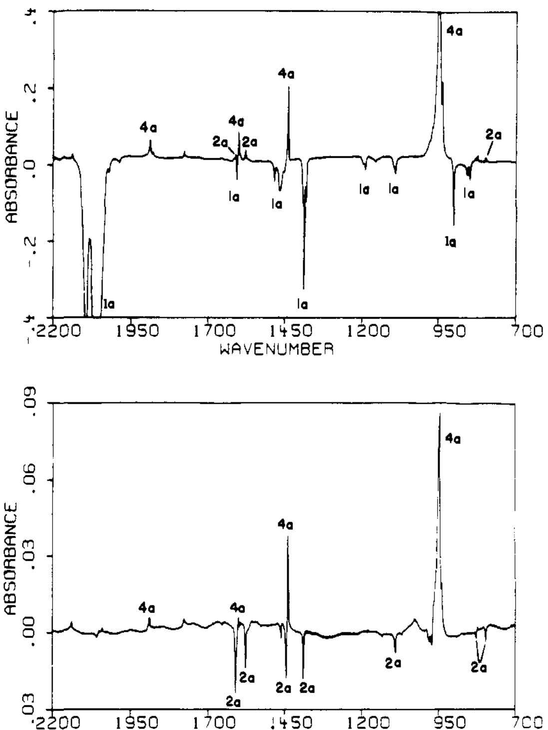


Figure 2. Top: IR difference spectrum showing spectral changes observed upon photolysis ($\lambda > 399$ nm. 16.3 h) of diazoethane (**1a**) (Ar. 8 K). The spectrum shows disappearance of **1a** and appearance of 3-methyldiazirine (**2a**) and ethene (**4a**). Bottom: IR difference spectrum illustrating the decrease of 3-methyldiazirine (**2a**) and concomitant increase of ethene (**4a**) upon 5.2 h of photolysis at $\lambda = 344 \pm 6.5$ nm (Ar. 8 K).

Results

Photolysis of Diazoethane (1a) in Argon. Long-wavelength irradiation of diazoethane (**1a**) in an argon matrix at 8 K produces ethene (**4a**: IR (Ar, 8 K) 3098 (m), 3077 (w), 2986 (m), 1889 (w), 1601 (m), 1440 (s), 1029 (w), 950 (vs), 938 (w), 827 (w) cm^{-1}) and a small amount of 3-methyldiazirine (**2a**: UV (Ar, 8 K) λ_{max} 344, 339, 335, 332, 327, 324, 319, 316, 312, 309 nm; IR (Ar, 8 K) 3044 (w), 2967 (w), 2934 (w), 2867 (m), 1610 (s), 1578 (s), 1462 (w), 1444 (m), 1389 (w), 1091 (w), 826 (w), 795 (w), 435 (w) cm^{-1}.)[27] The ratio of **4a**:**2a** is ca. 10:1. Figures 2 and 3 present IR and UV–vis spectra, respectively, which illustrate these transformations. Photolyses were performed at $\lambda > 472$ nm (50% conversion of **1a**, ca. 40 h) and $\lambda > 399$ nm (50% conversion of **1a**, ca. 6 h). IR absorptions of ethene were assigned by comparison with an authentic sample of ethene, matrix-isolated in argon at 8 K. (The electronic absorptions of ethene (λ_{max} 165 nm) lie outside the range of our spectrometer.) IR and UV–vis absorptions of 3-methyldiazirine (**2a**) were assigned by comparison to literature spectra.[24,28] The argon matrix UV spectrum of **2a**

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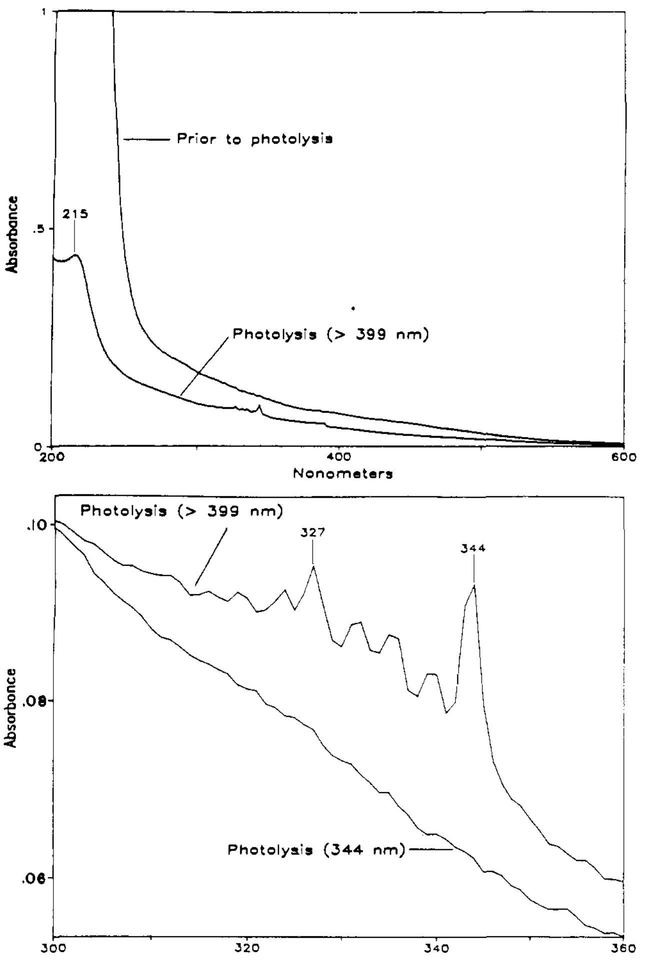

Figure 3. Top: UV–vis spectra before and after photolysis of diazoethane (**1a**) at λ > 399 nm (21 h), showing the formation of 3-methyldiazirine (**2a**). Absorption at 215 nm is due to residual diazoethane (**1a**). Bottom: Expanded spectrum showing the peaks due to **2a**. These transitions disappear upon irradiation at λ = 344 ± 6.5 nm.

(Figure 3) is red-shifted 2–3 nm from the reported gas-phase spectrum.[24] Diazoethane (**1a**) was subjected to the following sequence of photolysis conditions in argon at 15 K: λ > 497 nm (13.13 h), λ > 472 nm (9.25 h), and λ > 399 nm (9.00 h). ESR spectra recorded after each irradiation interval show no triplet transitions.

Brief irradiation of **1a** (λ > 200 nm) in argon at 8 K for 20 s and 1, 2.5, 5, and 10.3 min yields no species detectable by UV–vis spectroscopy. The 10.3-min photolysis results in nearly complete consumption of diazoethane, as monitored by UV–vis spectroscopy. Irradiation of **1a** (λ > 200 nm) in argon at 15 K for 1, 3, and 7 min yields no triplet species detectable by ESR spectroscopy.

Photolysis of 3-Methyldiazirine (2a) in Argon. 3-Methyldiazirine (**2a**) is generated in situ upon photolysis of diazoethane (**1a**) in argon at 8 K (vide supra). Subsequent narrow-band irradiation (λ = 344 ± 6.5 nm, 5.17 h) of **2a** results in complete conversion to ethene (**4a**) (Figure 2). Residual diazoethane present in the matrix is unreactive under these irradiation conditions. ESR spectra recorded during and after the photolysis show no triplet transitions. The relatively low concentration of **2a** in the matrices might render the IR or UV–vis signals of any minor photoproduct too faint to detect.

Photolysis of Diazoethane (1a) and 3-Methyldiazirine (2a) in Nitrogen. Irradiation of diazoethane (**1a**) (λ > 399 nm) in a nitrogen ($^{14}N_2$) matrix at 8 K yields ethene (**4a**) and 3-methyldiazirine (**2a**) (ratio ca. 10:1) at approximately the same rate of conversion as in argon (rigorous comparison of conversions is not valid because of variations in peak shapes and intensities from matrix to matrix). Photolysis of nascent 3-methyldiazirine (**2a**) (λ = 344 ± 6.5 nm, 4.83 h) produces ethene (**4a**) and a trace of diazoethane (**1a**), indicative of diazirine–diazo photoisomerization.[27] Irradiation of **1a** (λ > 472 nm, λ = 344 ± 6.5 nm, λ > 399 nm) in an isotopically labeled nitrogen ($^{15}N_2$) matrix at 8 K yields no incorporation of $^{15}N_2$ into diazoethane (**1a**) or 3-methyldiazirine (**2a**), as monitored by IR spectroscopy.

Diazoethane (**1a**) was subjected to the following sequence of photolysis conditions in nitrogen ($^{14}N_2$) at 15 K: λ > 472 nm (10.75 h), λ > 399 nm (8.00 h), and λ = 460 ± 6.5 nm (7.33 h). (The narrow-band photolysis conditions (λ = 460 ± 6.5 nm) were employed to minimize the possibility that the nascent ethylidene was itself being photolyzed.) ESR spectra recorded after each irradiation interval reveal no triplet transitions. Photolysis of **2a** (λ = 344 ± 6.5 nm, 3.5 h) also results in no triplet transitions.

Photolysis of Diazoethane (1a) and 2,2,2-Trideuteriodiazoethane (1b) in Xenon. Diazoethane (**1a**) was subjected to the following sequence of photolysis conditions in xenon at 15 K: λ > 472 nm (17.50 h), λ = 460 ± 6.5 nm (23.70 h), λ > 399 nm (7.58 h), λ = 344 ± 6.5 nm (13.25 h, photolysis of **2a**), λ > 200 nm (2, 4, and 6 min). ESR spectra recorded after each irradiation interval show no triplet transitions. 2,2,2-Trideuteriodiazoethane (**1b**)[29] was subjected to the following sequence of photolysis conditions in xenon at 15 K: λ > 472 nm (17.80 h), λ = 460 ± 6.5 nm (51.33 h), λ > 399 nm (5.38 h), λ = 344 ± 6.5 nm (4.75 h, photolysis of **2b**), λ > 200 nm (2, 4, and 8 min). ESR spectra recorded after each irradiation interval also reveal no triplet signals.

Photolysis of 2,2,2-Trideuteriodiazoethane (1b) and 3-(Trideuteriomethyl)diazirine (2b) in Argon. 2,2,2-Trideuteriodiazoethane (**1b**)[29] was subjected to the following sequence of photolysis conditions in argon at 15 K: λ > 497 nm (14.50 h), λ > 472 nm (11.67 h), λ = 460 ± 6.5 nm (11.50 h), and λ = 250 ± 6.5 nm (28.17 h). ESR spectra recorded after each irradiation interval show no triplet transitions.

Irradiation (λ > 399 nm, 5.5 h) of 2,2,2-trideuteriodiazoethane (**1b**)[29] produces some 3-(trideuteriomethyl)diazirine (**2b**), evidenced by the IR experiments in CO-doped argon matrices (vide infra). Subsequent narrow-band irradiation (λ = 344 ± 6.5 nm, 17.7 h) of **2b** results in no triplet transitions detectable by ESR spectroscopy.

Photolysis of Diazoethane (1a) and 2,2,2-Trideuteriodiazoethane (1b) in CO-Doped Argon. Irradiation (λ > 472 nm or λ > 399 nm) of either diazoethane (**1a**) or 2,2,2-trideuteriodiazoethane (**1b**)[29] in argon matrices doped with carbon monoxide (0.55% CO in Ar) generates small amounts of CO-trapped products, methylketenes **5** (**5a**, 2125 cm^{-1}, see Figure 4; **5b**, 2123 cm^{-1}), in addition to the corresponding ethenes **4** (**4b**: IR (0.55% CO in Ar, 8 K) 3051 (w), 2326 (w), 2275 (w), 2225 (w), 1285 (m), 1042 (w), 987 (w), 917 (m), 764 (m), 727 (m) cm^{-1}) and methyldiazirines **2** (**2b**: IR (0.55% CO in Ar, 8 K) 1597 (m), 1171 (w), 1051 (w) cm^{-1}). IR absorptions of ethene-d_3[30] and 3-(trideuteriomethyl)diazirine[28b] were assigned by comparison with literature spectra. Any differences in the relative amounts of **5a** and **5b** produced were less than our ability to quantify by IR spectroscopy. Identification of ketene **5a** was confirmed by comparison of its IR spectrum with that of the compound prepared independently by photochemical Wolff rearrangement of 1-diazo-2-propanone (**6**) (Scheme I). Irradiation of methyldiazirines **2** (λ = 344 ± 6.5 nm) also yields small amounts of ketenes **5** and diazoethanes **1**. Increasing the CO concentration (10% CO in Ar) results in a higher ratio of trapping product (ketene **5a**) to hydrogen migration product (ethene **4a**).

Thermolysis of Diazoethane (1a). Flash vacuum thermolysis (620 °C) of diazoethane (**1a**), followed by co-condensation with 0.58% CO in Ar at 30 K, generates only ethene (**4a**). IR absorptions attributable to 3-methyldiazirine (**2a**), methylketene (**5a**),

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(28) (a) Mitchell, R. W.; Merritt, J. A. *J. Mol. Spectrosc.* **1969**, *29*, 174–182. (b) Robertson, L. C.; Merritt, J. A. *J. Chem. Phys.* **1972**, *57*, 941–947.

(29) Sample consisted of ca. 80% 2,2,2-trideuteriodiazoethane and 20% 2,2-dideuteriodiazoethane. See Experimental Section.

(30) Machida, K.; Tanaka, Y. *J. Chem. Phys.* **1974**, *61*, 5040–5049.

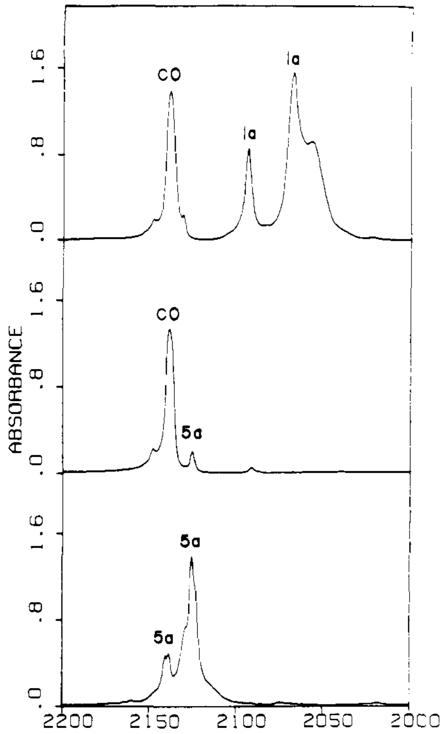

Figure 4. Top: Infrared spectrum of diazoethane (**1a**) in a 0.55% CO-doped argon matrix at 8 K. Middle: Infrared spectrum after photolysis ($\lambda > 472$ nm, 38 h, then $\lambda > 399$ nm, 7.8 h), producing ethene (**4a**), 3-methyldiazirine (**2a**), and methylketene (**5a**). The ketene stretch is visible at 2125 cm^{-1}. Bottom: Infrared spectrum of methylketene (**5a**), generated independently from photolysis ($\lambda > 363$ nm, 12 h) of 1-diazo-2-propanone (**6**) in an argon matrix at 8 K.

or ethylidene (**3a**) are not observed.

Photolysis of 1-Diazo-2-propanone (6). Irradiation ($\lambda > 363$ nm) of 1-diazo-2-propanone (**6**), matrix isolated in argon at 8 K, produces methylketene (**5a**: IR (Ar, 8 K), 3058 (w), 2958 (w), 2916 (m), 2140 (m), 2125 (vs), 1471 (w), 1447 (w), 1077 (w), 891 (w), 524 (m) cm^{-1}). Short-wavelength photolysis ($\lambda > 280$ nm) of methylketene (**5a**) slowly produces a trace of ethene (**4a**) as the only observable photoprocess.

Discussion

Scheme I summarizes the results of our attempts to generate and characterize ethylidene. Because of the low temperatures employed in our matrix-isolation experiments, reactive species virtually always exist in the lowest electronic state corresponding to a given geometry. Theory predicts that the ground electronic state of ethylidene is a triplet and that the triplet is a true energy minimum. Furthermore, the triplet possesses a high barrier to hydrogen migration. Thus, triplet ethylidene should be stable under our experimental conditions *if we devise a suitable route to it*. Both triplet methylene[31] and triplet 1-phenylethylidene[18] have been observed in matrices under analogous conditions. Triplet 1-phenylethylidene is stable at 10 K and does not suffer hydrogen migration until the matrix is warmed.[18] Triplet carbenes have been successfully characterized even in instances where hydrogen migration occurs from the triplet state.[17,18] In this instance, however, we were not able to observe either singlet or triplet ethylidene spectroscopically upon photolysis of diazoethane (**1a**) or 3-methyldiazirine (**2a**) at 8 K.

1,2-Hydrogen shifts in carbenes occur photochemically, as illustrated by the fact that triplet 1-phenylethylidene and triplet *o*-tolylmethylene undergo photochemical rearrangement much more rapidly than thermal rearrangement.[18] It is extremely unlikely, however, that our inability to observe either singlet or triplet ethylidene is due to secondary photolysis of an initially-formed carbene. We use the known electronic absorptions of singlet and triplet methylene as reasonable models for the corresponding absorptions of ethylidene. Triplet methylene absorbs only in the vacuum UV (<169 nm).[32] Thus, triplet ethylidene, if formed, should be stable under *all* of our photolysis conditions. ESR spectroscopy is a very sensitive probe for triplets; the fact that we do not observe a triplet signal suggests that triplet ethylidene is not formed. Singlet methylene absorbs in the visible (950–550 nm).[32] It is therefore unlikely that singlet ethylidene would be stable under any photolysis conditions that employed long-pass cutoff filters. However, photolysis of diazoethane-d_3 (**1b**) with bandpass irradiation ($\lambda = 460 \pm 6.5$ nm, $\lambda = 250 \pm 6.5$ nm) produces no detectable ethylidene (singlet or triplet). Either species should have survived the photolysis conditions. These conditions are similar to the conditions used to generate triplet di-*tert*-butylcarbene[33] and triplet diadamantylcarbene,[34] the only dialkyl carbenes to be characterized by ESR spectroscopy.

One hypothesis explaining our results is that singlet ethylidene is formed as a short-lived intermediate upon photolysis of both **1** and **2**, but the barrier to hydrogen shift is so low that intersystem crossing to the (stable) triplet state does not compete. The trapping experiments support the existence of a small barrier. Photolysis of diazoethanes **1a** and **1b** or diazirines **2a** and **2b** in CO-doped argon matrices results in formation of small amounts of ketenes **5a** and **5b**. Direct reaction of the excited states of **1** or **2** with CO seems unlikely (vide infra). Trapping is most readily explained in terms of an ethylidene intermediate.[35,36] This explanation requires that intermolecular trapping competes, to a small degree, with intramolecular hydrogen migration. We find that higher CO concentration gives increased yields of trapping products, which is also consistent with this explanation. We cannot determine the ratio of trapping to hydrogen shift because we do not known the relative extinction coefficients of the IR absorptions of ethene **4** and ketene **5**.

We employed two different strategies to make the rate of intersystem crossing in singlet ethylidene competitive with hydrogen migration: (i) increase the rate of intersystem crossing or (ii) decrease the rate of hydrogen migration. In an attempt to increase the rate of intersystem crossing via an external heavy-atom effect, we photolyzed diazoethane (**1a**) and 3-methyldiazirine (**3a**) in a xenon matrix. Our inability to observe a triplet ESR signal suggests that the xenon matrix failed to make intersystem crossing competitive with hydrogen migration. In an attempt to decrease the rate of hydrogen migration, we replaced the migrating hydrogen atom with deuterium. If a barrier to 1,2-hydrogen migration exists, then there is a possibility of slowing the migration due to a deuterium kinetic isotope effect.[37] Deuterium isotope effects can dramatically retard hydrogen shifts in carbenes at low temperatures, thereby totally altering reaction pathways.[18] Two experiments reveal no appreciable deuterium isotope effect in our study. First, comparison of the photolyses of either diazoethane (**1a**) and diazoethane-d_3 (**1b**) or 3-methyldiazirine (**2a**) and 3-(trideuteriomethyl)diazirine (**2b**) reveals no differences in terms of products observed, product ratios,

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(35) Methylene rapidly undergoes trapping reactions with both CO and N_2 in cryogenic matrices.[36a] This rapid recombination of CO and methylene explains the difficulty in photolyzing matrix-isolated ketene under conditions which yield rapid reaction in the gas phase.[36] This explanation could account for our observation that photochemical conversion of methylketene (**5a**) to ethene (**4a**) and CO is extremely slow. Moore and Pimentel also observed exchange of isotopic label upon photolysis of $H_2C^{15}N^{14}N$ in $^{14}N_2$, which they attributed to reaction of $^{14}N_2$ with methylene. We find no exchange upon photolysis of diazoethane (**1a**) in $^{15}N_2$.

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or photolysis rate. These results imply that the isotope effect does not retard hydrogen migration enough to allow intersystem crossing to occur. Second, both diazoethane (**1a**) and diazoethane-d_3 (**1b**) give similar yields of ketene trapping products (**5a** and **5b**) in CO-doped argon matrices. This result implies that the isotope effect does not retard hydrogen migration enough to allow more efficient trapping by CO.

A second hypothesis explaining our results is that ethylidene is formed from excited-state diazoethane with sufficient excess vibrational energy that it suffers hydrogen migration to produce ethene before the excess vibrational energy can be removed by the matrix.[38-40] In order to explore this possibility, we performed experiments employing N_2 as the matrix medium. Molecular dinitrogen would be able to absorb excess vibrational energy more readily than atomic argon, thereby quenching the vibrationally hot ethylidene and increasing the lifetime of singlet ethylidene enough to allow intersystem crossing to the triplet. The experiment failed to reveal triplet ethylidene by ESR spectroscopy and failed to reveal any new species by IR or UV-vis spectroscopy. Thus, we conclude either that vibrationally hot ethylidene is not the source of the problem or that a nitrogen matrix is ineffective at quenching vibrationally hot ethylidene.

A third hypothesis explaining our results holds that singlet ethylidene is not a true energy minimum and that hydrogen migration occurs without an activation barrier once nitrogen departs. This hypothesis is consistent with our observations that photolysis of diazoethanes **1** and 3-methyldiazirines **2** yield ethene with no detectable intermediate(s) and that these transformations show no significant isotope effect. The difficulty with this hypothesis arises in explaining the origin of the ketene (**5**) trapping products formed upon photolysis of **1** or **2** in CO-doped argon matrices. If this hypothesis is correct, CO must react with the excited state of **1** or **2** prior to nitrogen loss.

A fourth hypothesis explaining our results invokes hydrogen migration occurring in the singlet excited states of diazoethanes **1** and diazirines **2**. Tomioka[41] and Platz[42] previously suggested that hydrogen migrations occur in excited states of diazo compounds. The implication that a similar process occurs in excited states of diazirines is new. This hypothesis is consistent with our observations that photolysis of diazoethanes **1** and 3-methyldiazirines **2** yields ethene with no detectable intermediate(s) and that these transformations show no significant isotope effect. Again, the difficulty with this hypothesis arises in explaining the origin of the ketene (**5**) trapping products formed upon photolysis of **1** or **2** in CO-doped argon matrices. If this hypothesis is correct, CO must react with the excited state of **1** or **2** prior to nitrogen loss.

Mechanistic Implications for Ethylidene

Our key experimental observation concerning the intermediacy of ethylidene is ketene formation during the photolysis of **1** or **2** in CO-doped argon matrices. The most straightforward interpretation of this result postulates a trapping reaction between ethylidene and a carbon monoxide molecule that is suitably oriented in the host matrix. The reaction presumably occurs via singlet ethylidene. Singlet methylene is known to react with CO in the gas phase.[36] Although triplet carbenes react with CO at cryogenic temperatures,[43] triplet ethylidene is an unlikely precursor to ketene in this instance. If triplet ethylidene was formed, we should have been able to detect it by ESR spectroscopy in undoped matrices. This interpretation implies that the rate of 1,2-hydrogen migration in singlet ethylidene substantially exceeds the rate of intersystem crossing. The rate of intersystem crossing in singlet methylene in perfluorohexane solution is $\leq 8 \times 10^8$ s^{-1}.[44]

Again, we emphasize that other interpretations are possible, but seem less plausible to us. An alternate explanation postulates reaction of excited-state diazoethane or 3-methyldiazirine with a weak nucleophile, such as CO. The basis of Platz's pyridine ylide technique, however, rests on the fact that reasonably strong nucleophiles such as pyridine do *not* react with excited states of diazo compounds and diazirines.[21a]

Experimental Section

^{1}H NMR spectra were obtained with a Bruker WP-200 spectrometer. Chemical shifts are reported as ppm downfield from internal Me_4Si. Uncorrected melting points were determined with a Thomas-Hoover Unimelt apparatus. Mass spectral data were obtained with a Kratos MS-80RFA spectrometer (DS55/DS90 detector).

Infrared spectra were obtained on a Nicolet 740 FTIR instrument (MCT-B detector). Ultraviolet-visible studies employed a Hitachi U-3210 spectrometer. ESR experiments were performed on a Varian E-15 X-band spectrometer with a Varian E-101 microwave bridge. An EIP microwave counter (Model 625A CW) provided the microwave frequency.

Matrix-Isolation Spectroscopy. The apparatus and experimental technique for low-temperature matrix-isolation spectroscopy have been described previously;[45] however. some modifications have been made. The matrix-isolation apparatus for IR and UV-vis spectroscopy employed cryogenic refrigeration systems manufactured by CTI-Cryogenics (Model 22 refrigerator and Model 8300 compressor). The vacuum shroud and optical mounts were designed and manufactured by R. G. Hanson and Associates (Santa Barbara. CA). The window temperature is measured with a silicon diode sensor and regulated by a temperature controller (Scientific Instruments. Inc. Model 5500-1-25). The vacuum system consists of a diffusion pump (Edwards Model 63M) backed by a mechanical forepump (Welch Model 8814A) and a Pirani/Penning vacuum gauge (Edwards Model 1005). The pressure in the gas handling system is measured by a capacitance manometer (MKS Instruments. Inc. Type 122A). The matrix-isolation ESR apparatus differs from the previous description only in terms of the matrix support: a copper rod is used in place of a quartz rod. Finally. narrow band irradiation is provided by a Spectral Energy GM 252 monochromator.

Matrix:sample ratios are always maintained at ca. 500:1. but the absolute amount of sample deposited (i.e. the matrix thickness) depends on the intensity of the chromophore to be observed. Consequently. IR experiments typically require matrices of different thickness than UV experiments. Differences in matrix thickness lead to corresponding differences in photolysis times. ESR experiments are normally performed using the same matrix thickness as IR experiments.

The research grade gases for the matrices were purchased from the following vendors: argon (99.9995%). Liquid Carbonic and Matheson: nitrogen (99.9995%). AirCo: carbon monoxide (99.99%). AirCo: xenon (99.995%). Aga: isotopically labeled nitrogen ($^{15}N_2$. 99.6%). Isotec.

Sample Preparation. ***Caution***: Alkyl diazo compounds are highly reactive and often explosive. Synthesis and manipulation of these compounds requires extreme caution. A previous investigation of the photolysis of diazoethane was discontinued because of frequent detonations of the compound.[46] We encountered no serious problems during the synthesis and matrix deposition of diazoethane described below. In each instance. we worked with small quantities (<200 mg) of diazoethane. keeping the sample cold (≤-126 °C) and under vacuum or under dry nitrogen.

Acetaldehyde Tosylhydrazone.[47] Acetaldehyde (0.705 g. 16.0 mmol. Mallinckrodt) was added to a stirred slurry of *p*-toluenesulfonhydrazide (2.97 g. 16.0 mmol. Aldrich) in ethanol at 0 °C. The reaction mixture became homogeneous almost immediately. After 1-2 h. the tosylhydrazone precipitated from solution. It was isolated by suction filtration. washed with cold hexane. and dried in vacuo to yield 2.10 g (62%): mp 84-85 °C: ^{1}H NMR ($CDCl_3$) δ 1.78 and 1.90 (both d. 3 H: syn and anti isomers of the hydrazone). 2.43 (s. 3 H). 6.88 and 7.20 (both q. 1 H: two isomers). 7.30-7.9 (m. 4 H): mass spectrum. *m/z* (relative intensity) 212 (M^+. 0.5). 171 (19). 157 (12). 155 (24). 140 (26). 139 (40). 107 (23). 92 (65). 91 (100). 65 (75).

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(39) For an example of this phenomenon. see: LeBlanc. B. F.: Sheridan. R. S. *J. Am. Chem. Soc.* **1988**. *110*. 7250-7252.

(40) This process would probably occur on the singlet surface. but our analysis applies equally well to the triplet surface.

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Acetaldehyde Tosylhydrazone, Sodium Salt. A dispersion of 60% NaH/mineral oil (1 equiv; Aldrich) was added to a stirred solution of the tosylhydrazone (ca. 0.25 g) in 20 mL of CH_2Cl_2. After 1 h. 25 mL of pentane was added. causing the salt to precipitate as a sticky. off-white solid. The salt was collected by suction filtration. washed with cold hexane. and dried in vacuo. The product. obtained in quantitative yield. was crushed to a fine powder and used without further purification.

Diazoethane (1a). The freshly prepared tosylhydrazone salt was placed in a 10-mL round-bottomed flask. A glass adapter arm (essentially a short-path distillation column) connected the flask to a collection tube. The system was evacuated (<1 Torr). and the salt was heated to 40 °C for 30 min with use of a silicone oil bath. Pyrolysis was then effected by raising the temperature to 95 °C for 90 min. The yellow-orange diazoethane condensed in the collection tube. which had been cooled with liquid N_2. The liquid N_2 bath was replaced with a methylcyclohexane slush bath (−126 °C). and the system was vented with dry N_2. After the collection tube was transferred to the matrix isolation apparatus. the sample was subjected to 3 freeze–pump–thaw cycles at −126 °C (the sample was not allowed to warm above ca. −100 °C). After the pressure in the matrix-isolation system had fallen below 5×10^{-6} Torr. diazoethane was sublimed from the −126 °C slush bath and codeposited with either argon or N_2 on a cold window maintained at 30 or 24 K. respectively. ^{1}H NMR ($CDCl_3$) δ 1.77 (d. 3 H. $J = 5.5$ Hz). 3.39 (q. 1 H. $J = 5.5$ Hz):[48] UV (CH_3CN. 298 K) λ_{max} 222. 468 nm:[46,49] UV (Ar. 9 K) λ_{max} 215 nm; IR (Ar. 8 K) 3091 (m). 2989 (w). 2955 (m). 2907 (m). 2866 (w). 2094 (s). 2063 (vs). 1606 (m). 1482 (w). 1462 (w). 1440 (m). 1388 (m). 1092 (w). 900 (m). 852 (w). 581 (m). 454 (m). 418 (m) cm^{-1}.

2,2,2-Trideuterioacetaldehyde was prepared by pyridine-catalyzed exchange of deuterium (from D_2O) for hydrogen in acetaldehyde.[50] ^{1}H NMR showed the product to be 80% acetaldehyde-d_3 and 20% acetaldehyde-d_2 ($CDCl_3$): δ 2.18 (m [1:3:5:5:3:1]. 1 H. $J = 3$ Hz. CHD_2CHO). 9.80 (br s. 4.8 H. $CHD_2CHO + CD_3CHO$). (A ratio of 1:3:5:5:3:1 requires that $^3J_{H-H} \approx {}^2J_{H-D}$).

2,2,2-Trideuterioacetaldehyde tosylhydrazone was synthesized in 77% yield using the procedure described for the protiated analog. Mp 84–85.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.43 (s. 3 H). 6.87 and 7.19 (both br s. 1 H: syn and anti isomers of hydrazone). 7.32 (dd. 2 H). 7.44 and 7.53 (both s. 1 H: two isomers): 7.84 (dd. 2 H); mass spectrum. m/z (relative intensity) 215 (M^+. 0.9). 214 (0.5). 173 (14). 172 (14). 155 (41). 141 (25). 140 (17). 139 (44). 109 (21). 108 (24). 107 (18). 93 (58). 92 (63). 91 (100).

2,2,2-Trideuteriodiazoethane (1b) was prepared using the procedure described for the protiated analog: IR (0.55% CO in Ar. 8 K) 3088 (m). 2216 (m). 2065 (vs). 1947 (m). 1385 (s). 1109 (w). 1058 (w). 547 (m) cm^{-1}.

1-Diazo-2-propanone (6) was prepared from pentane-1.3-dione by diazo transfer reaction with *p*-carboxybenzenesulfonazide (Aldrich) followed by basic hydrolysis.[51] ^{1}H NMR ($CDCl_3$) δ 2.11 (br s. 3 H). 5.25 (br s. 1 H): IR (Ar. 9 K) 2109 (vs). 2088 (m). 1669 (s) cm^{-1}. The compound was sublimed at −63 °C ($<5 \times 10^{-6}$ Torr) and codeposited with argon to form a matrix.

Note Added in Proof. Diazoethane (**1**) was subjected to the following sequence of photolysis conditions in a methylcyclohexane glass at 4.2 K: $\lambda > 237$ nm (1 h), $\lambda > 399$ nm (2 h), $\lambda = 460 \pm 6.5$ nm (2.4 h). ESR spectra recorded after each irradiation interval reveal no triplet transitions. As in the case of N_2 matrices (vide supra), we conclude either that vibrationally hot ethylidene is not the cause of our inability to observe triplet ethylidene (**3**) or that a methylcyclohexane matrix is ineffective at quenching vibrationally hot ethylidene.

Gallo and Schaefer recently computed a singlet–triplet splitting of 5 ± 1 kcal/mol for ethylidene (**3**) (Gallo, M. M.; Schaefer, H. F., III *J. Phys. Chem.* **1992**, *96*, 1515–1517).

Acknowledgment. We gratefully acknowledge the National Science Foundation for research support (CHE-9003319). R.J.M. is the recipient of an NSF Presidential Young Investigator Award (CHE-8957529), a 3M Nontenured Faculty Grant Award, and a DuPont Young Faculty Grant. We thank Professor M. S. Platz (Ohio State University) for a preprint concerning excited state processes on dialkyldiazirines.

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Framework Crystal Structure Solution by Simulated Annealing: Test Application to Known Zeolite Structures

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Contribution from Exxon Research and Engineering Company. Route 22 East. Annandale. New Jersey 08801. and BIOSYM Technologies Inc.. 9685 Scranton Road. San Diego. California 92121-2777. *Received April 15. 1991*

Abstract: Direct. real-space solution of zeolite framework crystal structures by simulated annealing has been explored as an alternative to conventional powder diffraction or model-building methods. The method. as well as its success in predicting the framework structures of known zeolites. is described in detail. Data taken as input to the method are unit cell dimensions. symmetry. and framework density. The general geometrical characteristics of the 4-connected framework structures of zeolite materials are captured by a figure of merit that contains terms based on T–T distances (T = tetrahedral species. Si or Al etc.). T–T–T angles and average angles. degree of T-atom coordination. appearance of 3-connectedness in projection. and cylindrical or spherical pore size. Test solutions of 64 known zeolite structures with 6 or fewer unique T-atoms give a successful result in 57 cases. Low-symmetry systems, in particular. tend to give rise to large numbers of hypothetical 4-connected structures that satisfy the geometrical considerations. and in total. more than 5000 hypothetical structures have been produced. The observed structure usually ranks among those with the lower values of the figure of merit. Incorporation of a sample-specific contribution to the figure of merit based on the degree to which the model matches a target powder diffraction pattern improves the success of the method. This additional term almost invariably causes the observed. known structure to have the lowest value of the figure of merit. and it is thus a great aid in practical structure solution.

1. Introduction

Structure solution continues to be a taxing aspect of the characterization of crystalline materials that occur only in polycrystalline form (i.e. in which individual crystallite sizes are smaller than some 10 μm). The past decade has seen substantial improvements in both neutron and X-ray diffraction methods, notably in the use of synchrotron X-radiation,[1] but initial solutions of the

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