National Science Foundation for a Presidential Young Investigator Award (Grant CHE-8552735).

Supplementary Material Available: Full NMR, IR, and mass spectral data and C, H, N analysis information for compounds **1–13** (6 pages). Ordering information is given on any current masthead page.

Pyrolysis of Acetylene: A Thermal Source of Vinylidene

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Received November 21, 1986

Nonempirical molecular orbital calculations reveal that vinylidene exists in shallow (~4 kcal/mol) minimum of the C_2H_2 potential energy surface at about 40 kcal/mol above ground-state acetylene; on the other hand, dynamical considerations, tunneling included, set an upper limit of about 10 ps for its lifetime toward rearrangement to acetylene.[1-4] Rational skepticism thus prevails about the possibility of detecting such species either by chemical or spectroscopic means. The recent finding that the CH_2 scissors and C=C stretching vibrations of $H_2C{=}C^{2\bullet}\ {}^1A_1$ can be excited up to 12 kcal/mol by electron photodetachment of its anion does not really improve the prospects since an even shorter time scale is involved in such event.[5] In this connection the thermal intramolecular scrambling observed in the system $HC{=}{}^{13}CDC{=}DC{=}{}^{13}CH$, which apparently requires a discrete symmetrical intermediate resembling vinylidene, looks more auspicious.[6] We now report the results of kinetic and trapping experiments performed in acetylene/benzene and acetylene/toluene mixtures above 820 K by modulated beam dynamic mass spectrometry which provide direct evidence of vinylidene participation in chemical reactions. Under such conditions the fast equilibrium

$$HC{=}CH \rightleftarrows H_2C{=}C^{2\bullet} \qquad (1, -1)$$

precedes carbene addition to the aromatic ring thereby circumventing kinetic restrictions arising from the short lifetime of vinylidene.

Pyrolyses were carried out in a 122-cm^3 fused silica reactor coupled to a on-line modulated beam mass spectrometer (EMBA II, Extrel) via a molecular leak. An all-glass mixer was used to homogenize gas mixtures prior to expansion into the heated reactor. This setup was adequate for the continuous monitoring of reactants and products including labile or unvolatile species. Reproducible kinetic results could be routinely obtained by alternating "conditioning" pyrolyses at about 200 K above reaction temperatures. Acetylene was purified by passage through water and subsequently distilled at −90 °C. Reagent grade benzene and toluene were further purified by vacuum distillation. Ethylene (Matheson) was used as received. Second-order rate constants for the decomposition of neat acetylene up to 50% conversions as well as those derived from its pseudo-first-order decay in about 10-fold excess of benzene or toluene are shown in Figure 1. All are very similar in the range 820–970 K, leading to an average activation energy of 37 ± 2 kcal/mol in accord with earlier measurements for acetylene pyrolysis.[7] This clearly suggests a common mechanism, further confirmed by product analyses. Thus the self-reaction of C_2H_2 leads first to vinylacetylene but soon evolves into benzene whose fragment at *m/z* 52 overlaps the molecular ion of C_4H_4.[8] Proper analysis of the composite signal indicates that the concentration of C_4H_4 initially rises and then levels off, revealing decomposition or further reaction with C_2H_2. On the other hand, the mass spectra of reacting C_2H_2:C_6H_6 mixtures display a series of major products at *m/z* 78 + 26*n*, *n* = 1, 2, 3, and 4 (Figure 2a). Since benzene is verifiably stable under all conditions, these species obviously involve the sequential addition of C_2H_2 and are tentatively assigned to polyvinyl benzenes, both for kinetic and thermodynamic reasons and on the basis of the conspicuous pattern of M^+, $(M - 1)^+$, *and* $(M - 2)^+$ signals also observed in the reported mass spectra of divinyl benzenes.[9-12] When toluene replaces benzene, large signals at *m/z* 117 and 118 (*but not at m/z 104*), corresponding to methyl styrene isomers, appear early in the course of reaction (Figure 2b).[9] In this case the higher reactivity of toluene (see Figure 1) apparently prevents further addition of C_2H_2 units past the first step, strongly suggesting the electrophilic nature of the intermediate involved.[13] The crucial issue of whether this is the vinyl radical or a reactive isomer of acetylene such as $H_2C{=}C^{2\bullet}$ or a triplet state ${}^3C_2H_2$ is now addressed. Since ethylene is known to undergo thermal disproportionation into vinyl and ethyl radicals, it was thought that the identity of the products formed by decomposing ethylene in excess totoluene should provide a clue to this question.[14] Now in addition to methylstyrene, *styrene itself m/z 104*, divinyl benzenes *m/z* 130, and traces of methylethylbenzene *m/z* 120 were also detected (Figure 2c). The new species certainly derive from vinyl radical displacement of the methyl group in toluene and methyl styrenes, a process otherwise inaccessible to carbenes.

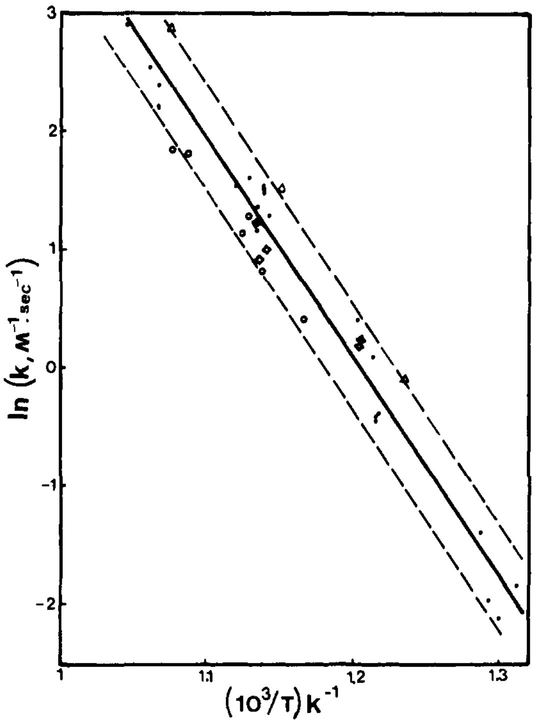

Figure 1. Rate constants for reaction between $2C_2H_2$ (•), $2C_2H_2$ in excess of N_2 (□), C_2H_2 + C_6H_6 (○), and C_2H_2 + $C_6H_5CH_3$ (△) as function of temperature. Broken lines correspond to ($k \pm 2\sigma$).

We have recently shown that a vinyl radical chain mechanism for acetylene thermal dimerization is untenable on kinetic and

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[1] Scheiner, A. C.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1985**, *107*, 4451.

[2] Osamura, Y.; Schaefer, H. F., III; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904.

[3] Skell, P. S.; Fagone, F. A.; Klabunde, K. J. *J. Am. Chem. Soc.* **1972**, *94*, 7862.

[4] Chen, Y.; Pique, J. P.; field, R.; Kinsey, J., paper to be presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 5–10, 1987.

[5] Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *Chem. Phys. Lett.* **1983**, *100*, 124.

[6] Brown, R. F. C.; Eastwood, F. W.; Jackman, G. P. *Aust. J. Chem.* **1978**, *31*, 579.

[7] Back, M. H. *Can. J. Chem.* **1971**, *49*, 2199.

[8] Cullis, C. F.; Franklin, N. H. *Proc. R. Soc. London, A* **1964**, *280*, 139.

[9] Stenhagen, E.; Abrahamson, S.; McLafferty, F. W. *Registry of Mass Spectral Data*; Wiley: New York, 1974; Vol. 1.

0002-7863/87/1509-3154$01.50/0

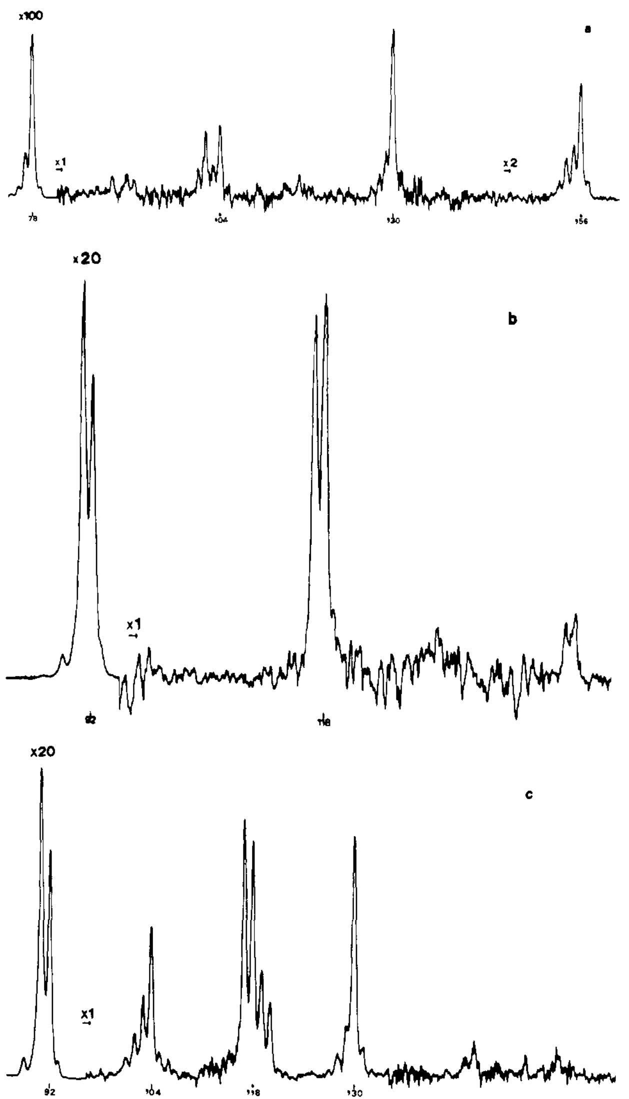

Figure 2. Mass spectra, 50 eV, of reacting mixtures of (a) C_2H_2 (0.13)/C_6H_6 (0.87) at 49 torr, 942 K; (b) C_2H_2 (0.3)/$C_6H_5CH_3$ (0.7) at 32 torr, 942 K; and (c) C_2H_4 (0.3)/$C_6H_5CH_3$ (0.7) at 53 torr, 942 K, at early stages.

thermochemical grounds.[15] After considering that formation of the lowest lying triplet state of acetylene is about 80 kcal/mol endothermic, we finally proposed the intermediacy of vinylidene.[16] On the basis of the above evidence we conclude that this is indeed the case and that acetylene pyrolyses studied here can be described by a scheme comprising steps (1,−1) followed by addition/insertion reactions

$$H_2C{=}C^{2\bullet} + RCH{=}CHR' \rightarrow H_2C{=}CH{-}CR{=}CHR' \qquad (2)$$

with $r_{-1} \gg r_2$, $E_2 = 0 \pm 1$ kcal/mol, $E_a = \Delta H_1 + E_2$, and $\Delta H_1 = 37$ kcal/mol, in good agreement with theoretical predictions.[1,2,17] Further work is under way.

Acknowledgment. We are grateful to CIC and CONICET of Argentina for financial support.

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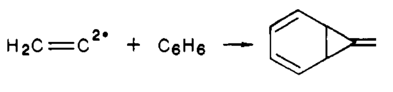
[10] The estimated heat of formation of 7-methylenebicyclo[4.1.0]hepta-2,4-diene (A),[11] the primary product of vinylidene addition to benzene



(3)

$\Delta H_{f,300K}$ (A) = 90.2 kcal/mol leads to $\Delta H_3 = -23$ kcal/mol and to $\Delta H_4 = -55$ kcal/mol for its isomerization to styrene: $A = C_6H_5C_2H_3$.[12]

[11] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[12] Brinker et al. (Brinker, U. H.; König, L. *J. Am. Chem. Soc.* **1981**, *103*, 212) report that the closely related isomerization of 7-methylenebicyclo[4.1.0]hept-2-ene to vinylcyclohexa-1,3-diene takes place readily at temperatures as low as 200 °C.

[13] Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

[14] Ayrancy, G.; Back, M. H. *Int. J. Chem. Kinet.* **1983**, *15*, 83.

[15] Durăn, R. P.; Amorebieta, V. T.; Colussi, A. J., submitted for publication in *J. Phys. Chem.*

[16] Wetmore, R. W.; Schaefer, H. F., III *J. Chem. Phys.* **1978**, *69*, 1648.

[17] Canosa-Mas et al. (Canosa-Mas, E. C.; Frey, M. H.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 283) have measured a value of $k = 1.5 \times 10^{11}$ M^{-1} s^{-1} for the reaction $^1CH_2 + C_2H_2 \rightarrow C_3H_4$ at 300 K.

The First Nonenzymic Stereospecific Intramolecular Reduction by an NADH Mimic Containing a Covalently Bound Carbonyl Moiety

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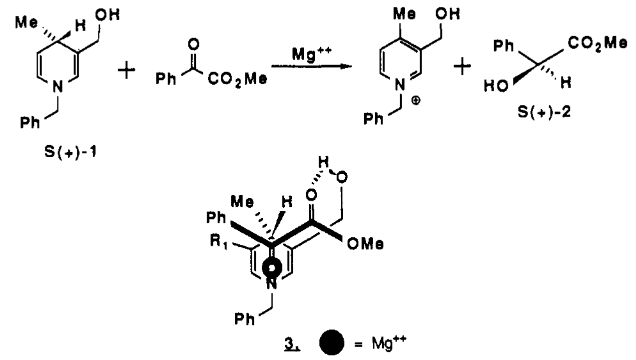
Received November 14, 1986

We have recently described[1] the pure self-immolative chirality transfer between the stereochemically defined (*S*)-*N*-benzyl-3-(hydroxymethyl)-4-methyl-1,4-dihydropyridine (**1**) and benzoylformic ester. The methyl mandelate (**2**) produced was found to be greater than 95% enantiomerically pure (corrected for the enantiomeric purity of **1**) and possessed the *S* configuration. This process, which occurred in the absence of any external or appended stereocenters, other than that present in the 4-position of **1**, was assumed to occur via the previously suggested ternary complex **3** consisting of **1**, benzoyl formic ester, and the magnesium ion. The stereochemical outcome was rationalized by assuming a hydrogen bond or dipole–dipole interaction between the hydroxyl group and the carbomethoxyl group in **3**, resulting in hydride transfer to the *re* face of the carbonyl group. In the natural NADH–NAD$^+$ system the 4-position is achiral containing two hydrogens and the enzyme, alcohol dehydrogenase, must be employed.[2] An enormous quantity of work has been done with metal ions (Mg^{2+}, Zn^{2+}) in place of the enzyme in an effort to mimic the natural process and, along with successful redox behavior, impressive stereochemical control has been achieved.[3] However, the metal ion mediated reductions of prochiral carbonyls to optically enriched carbinols required several days to reach completion, in dramatic contrast to the rate of the enzyme's rapid catalytic activity. Thus, these studies have been more mechanistically interesting rather than synthetically useful processes.



We now wish to report that we have succeeded in carrying out an *intramolecular* version of this metal ion mediated reduction

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[1] Meyers, A. I.; Oppenlaender, T. *J. Am. Chem. Soc.* **1986**, *108*, 1989.

[2] Fischer, H. F.; Westheimher, F. H.; Conn, E. E.; Vennesland, B. *J. Am. Chem. Soc.* **1951**, *73*, 2403.

[3] For summaries of metal ion mediated NADH mimics for stereochemical reduction of prochiral carbonyls, see: (a) Ohno, A. *ACS Symp. Ser.* **1982**, *No. 185*, 1. (b) Ohno, A.; Lee, J. H.; Yasuma, T.; Oka, S. *Tetrahedron Lett.* **1984**, *25*, 1995. (c) Inouye, Y.; Oda, J.; Baba, N. *Asymmetric Synthesis*; Academic: New York, 1983; Vol. 2, p 1. (d) Kellogg, R. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 782. (e) Ohno, A.; Vishida, S. *Lecture Notes in Bioorganic Chemistry*; Springer Verlag: Heidelberg, 1986.