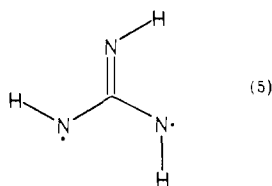


Very slow cooling of pure molten iminotetrazoline **1a** in a sample tube during several weeks produced a clear (single?) crystal. Irradiation of this crystal at -195°C for 1 min produced two rather strong signals the appearance of which was very dependent upon the orientation of the sample in the magnetic field as expected. At an orientation which gave the most symmetrical hyperfine pattern, the low-field multiplet again consisted of at least nine equally spaced lines separated by 11.7 ± 0.5 G. The striking similarity of the single crystal spectrum to the $\Delta m = 2$ transition of randomly oriented triplets is already known from trimethylenemethane. Since the spectrum was centered at $\sim 3108 \pm 10$ G, it must correspond to alignment of the xy plane of the crystal with the magnetic field. Probably, the sample had crystallized with the z axis running the length of the tube similar to the precursor of trimethylenemethane, 3-methylenecyclobutanone.⁵

The assignment of the tris(imino)methane structure **3** to the species responsible for the ESR spectrum is based on the resemblance of the spectrum to that of trimethylenemethane ($|D/hc| = 0.025 \text{ cm}^{-1}$),^{2a} the size of the zero-field splitting parameter, and the changes, especially of the hyperfine pattern of the $\Delta m = 2$ transition, on deuteration of **1a**. In terms of a dipole approximation,⁹ the observed zero-field splitting parameter D/hc corresponds to an average separation of the unpaired electrons of 3.4 \AA , in reasonable agreement with the proposed structure **3**. Introduction of one $[\text{D}_3]$ methyl group as in **1b** and **4a** resulted in partial loss, and perdeuteration, as in $[\text{D}_9]$ -**1a**, caused complete disappearance of the hyperfine structure of the $\Delta m = 2$ transition. Concomitantly, the expected sharpening of the xy lines was observed (Figure 1).

Splitting of both the supposed single-crystal spectrum and the $\Delta m = 2$ transition into at least nine lines proves that, as well as the nitrogen atoms, the protons are also involved in coupling. In general, the hydrogens of a methyl group attached to a nitrogen should have a coupling about twice as large as the nitrogen itself.¹⁰ A complete geometry optimization of **5** by INDO calculations produced a structure of C_{3h} symmetry having the parameters $\text{C-N} = 1.357 \text{ \AA}$, $\text{N-H} = 1.073 \text{ \AA}$, and $\angle\text{CNH} = 112.6^{\circ}$, and the coupling constants $a^{\text{N}} = 11.3$ and $a^{\text{H}} = -19.8$ G. Using the optimized geometry of **5** and sub-



stituting the optimized methyl group parameters obtained previously,¹¹ one obtains for **3** $a^{\text{N}} = 11.4$ and $a^{\text{H}} = 25 \pm 1$ G. Bending of the methyl groups out of the plane in order to account for possible steric interactions only slightly influenced the coupling constants. Thus, even at an assumed dihedral angle of 45° , the INDO calculation afforded $a^{\text{N}} = 10.9$ and $a^{\text{H}} = 25$ G. However, computer simulation of the ESR spectrum of **3** using $a^{\text{N}} = 11.7$ and $a^{\text{H}} = 23.4$ G did not give a satisfactory agreement with the observed spectra. Surprisingly, the computer-generated 16-line spectrum on the basis of $a^{\text{N}} = a^{\text{H}} = 11.7$ G, the inner eight lines of which represent $>95\%$ of its total intensity, did agree much better with the experimental spectra. For comparison, the INDO-optimized geometry of trimethylenemethane, which had yielded the expected planar D_{3h} structure and the parameters $\text{C-C} = 1.395 \text{ \AA}$,¹² $\text{C-H} = 1.114 \text{ \AA}$, and $\angle\text{HCH} = 112.2^{\circ}$, afforded a coupling constant $a^{\text{H}} = -18.9$ G. In view of the experimental value of $|a^{\text{H}}| = 9.17$ G,^{2a} the INDO approximation does not satisfactorily predict the value of a^{H} for trimethylenemethane, which may reflect exaggerated calculated couplings for the tris(imino)methane **3**.

When the *tert*-butyl substituted iminotetrazolines **1c** and **4b**, respectively, were irradiated in a butyronitrile matrix, the observed triplet ESR spectra closely resembled that of **3** but were of lower intensity. Irradiation of both **1d** and **1e** in hexafluorobenzene at -195°C produced only monoradicals.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for support of this work. W.C.D. acknowledges donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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Energetics of the Thermal Polymerization of a Diacetylene Crystal

Sir:

There has been a great deal of interest recently in the solid-state polymerization of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate), PTS.¹ Interest in this particular diacetylene has two principal origins: (1) thermal polymerization of PTS yields quantitative conversion to a fully conjugated polymer single crystal and (2) the conversion vs. time curve (obtained by monomer extraction) is S shaped—a result of a dramatic autocatalytic effect observed at $\sim 10\%$ conversion to polymer.² The autocatalytic effect almost certainly has its origins in the strain energy associated with the formation of the polymer/monomer solid solution.^{1,3} However, a complete understanding of this effect requires a more detailed analysis of the energetics of the polymerization process as well as a reliable determination of the increase in polymerization rate in the autocatalytic region, i.e., a determination of $\gamma_{\text{max}}/\gamma_0$ where γ_0 is the polymerization rate at low conversion and γ_{max} is the maximum rate in the autocatalytic region. Monomer extraction measurements are not accurate enough to determine $\gamma_{\text{max}}/\gamma_0$, while recent spectroscopic work¹ has yielded only a lower limit, $\gamma_{\text{max}}/\gamma_0 > 10$.

In this communication, we present a preliminary report on the thermal polymerization of PTS studied by differential scanning calorimetry (DSC). We determine the heat of polymerization, ΔH_p , and discuss briefly the energetics and mechanism of diacetylene polymerization. We also present a

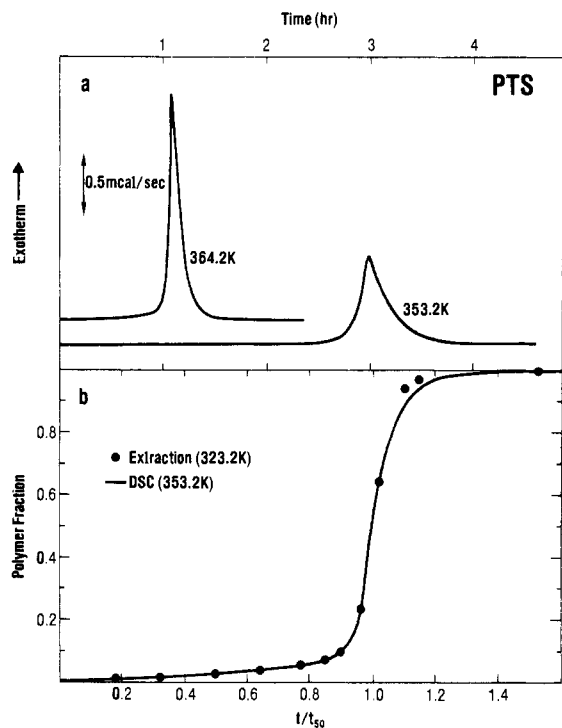


Figure 1. (a) Typical isothermal DSC scans showing the exothermic polymerization of PTS monomer. The sample weights are 10.54 and 10.99 mg for the 364.2 and 353.2 K curves, respectively. (b) Polymer fraction vs. time obtained from the 353.2 K DSC curve and compared with extraction results at 323.2 K. The t_{50} normalization constant is the time required to reach 50% polymer: $t_{50} = 3.02$ h at 353.2 K and 62.6 h at 323.2 K.

quantitative measurement of γ_{\max} as well as γ_{\max}/γ_0 . A Perkin-Elmer DSC-2 with automated data processing was employed for all results presented here. All measurements were carried out under an argon atmosphere. PTS was prepared using a slightly modified version of Wegner's procedure.²

Typical isothermal DSC scans are shown in Figure 1a. The reaction is exothermic^{4,5} with a long "induction period" consistent with the extraction measurements. The differential power at any point on these curves is directly related to the polymerization rate, $\gamma = d[P]/dt$ where $[P]$ is the polymer fraction; the integral under these curves yields the heat of polymerization, ΔH_p , since the reaction is quantitative. Care must be taken in choosing the baseline for analysis, however, since it is well established that PTS polymerizes during the "induction period" at a slow, constant rate.^{1,2} We chose to adjust the baseline by fitting previous conversion results⁶—the conversion in the DSC experiments being obtained from the integral of the DSC curve up to a time t , divided by the total integral. Results are shown in Figure 1b. (The final baseline adjustment from the constant level region of Figure 1a was 0.004 mcal/s.) The fit is quite good, except in the high conversion region where the extraction results are most suspect.⁶ We find $\Delta H_p = -36.5$ kcal/mol from the 353.2 K curve and -36.7 kcal/mol following a similar procedure for the 364.2 K curve. In addition, 8 separate determinations of ΔH_p (from a programmed temperature technique which avoids the baseline problem) have yielded -36.4 ± 0.5 kcal/mol. We have also calculated ΔH_p using a bond energy/bond length relationship from Dewar⁷ and the observed PTS bond lengths.⁸ We find -31.5 kcal/mol in quite reasonable agreement with experiment. The energy difference between the acetylene backbone ($=RCC\equiv CCR=$), which is observed for TPS polymer, and the butatriene backbone ($-RC=C=C-CR-$) is insignificant (<0.5 kcal/mol) with this simple calculation.

The polymerization rate, γ , can be determined from the height, h , at any point along the DSC curves as $\gamma = hM/w(-\Delta H_p)$, where M is the molecular weight of PTS monomer (418) and w is the sample weight. Therefore, γ_{\max} is directly accessible. The temperature dependence of γ_{\max} (343 to 364 K) yields an activation energy, E_a , of 22.5 ± 0.5 kcal/mol in excellent agreement with other measurements^{1,6} at both low and high conversions. (E_a is primarily associated with the initiation event.¹) Fixing E_a at 22.5 kcal/mol, we find

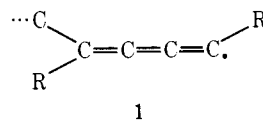
$$\gamma_{\max} = (6.15 \pm 0.15) \times 10^{10} \exp(-E_a/RT) \text{ s}^{-1} \quad (1)$$

and

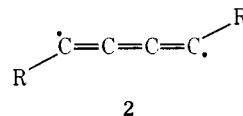
$$\gamma_0 = (3.55 \pm 0.45) \times 10^8 \exp(-E_a/RT) \text{ s}^{-1} \quad (2)$$

where the latter result comes from low conversion extraction experiments.⁹ Thus, we have $\gamma_{\max}/\gamma_0 = 175 \pm 25$.¹⁰ It has been suggested previously¹ that the entire autocatalytic effect can be attributed to an increase in the propagation length of the chains. A lower limit of 24 repeat units ($=RCC\equiv C-CR=$)_n has been estimated for the chain length in the low conversion limit.¹ If the preceding arguments are correct, the lower limit for the chain length in the high conversion region is 4200 repeat units or a chain length $>2 \mu\text{m}$! A more detailed theory for the autocatalytic effect is required before this result can be taken seriously, however.

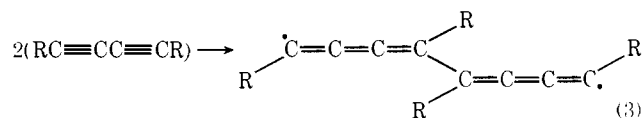
The evaluation of ΔH_p ($= -36.6$ kcal/mol $= -1.6$ eV) provides an important missing link in the analysis of the energetics of diacetylene polymerization. Since the chains are obviously very long, the addition of one monomer unit to a "living" chain end of form **1** will be exothermic by 1.6 eV. The



addition of a monomer unit in its lowest energy excited state, M^* , which can be represented as trans structure¹¹ **2**, should



be exothermic by ~ 4.1 eV, i.e., a sp^2 - sp^2 σ bond energy.⁷ It follows then that $M \rightarrow M^*$ requires ~ 2.5 eV (a reasonable value for the triplet state of the monomer)¹² and that reaction



3, which we imagine to be the initial step in polymerization, is uphill by about +0.9 eV (~ 21 kcal/mol). It is straightforward to show that the above dimerization is thermally allowed from molecular orbital considerations.¹³ Therefore, since the barrier for the further propagation is low,⁶ the activation energy for chain initiation will be predicted to be ~ 0.9 eV in good agreement with the observed value of 1.0 eV. An alternative (and perhaps more popular) scheme would involve the initial generation of the bicarbene dimer species.¹⁴⁻¹⁶ This scheme yields an unacceptably high E_a value of ~ 2.5 eV with a similar construction. Though these arguments obviously oversimplify the problem, we believe the direction for future theoretical calculations of the reaction energetics and pathway is clearly indicated. It seems clear from these energetic arguments that vibrational excitation of the ground state provides a quite reasonable pathway for the thermal process. Previously proposed, and much discussed, excited state mechanisms for

thermal polymerization are both unnecessary and unreasonable energetically.

Acknowledgment. One of us (R.C.) acknowledges a helpful discussion with Professor D. M. Lemal.

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A Selective Formose Reaction¹

Sir:

The formose reaction, by which a complex mixture of sugars and sugar alcohols (the so-called formose) is produced by the base-catalyzed condensation of formaldehyde, has received much attention in connection with the prebiotic synthesis of carbohydrates and the microbial utilization of formose sugars.²⁻⁴ The reaction using calcium hydroxide catalyst in aqueous media, which has been most widely investigated, proceeds via three distinct steps. (1) An induction period is necessary for the formation of a small amount of condensation products of C_2 and C_3 such as glycolaldehyde, glyceraldehyde, and dihydroxyacetone, which are believed to act as catalytic species by complexing with calcium ions, in the subsequent step. (2) Formose formation occurs rapidly and the yield of formose sugars reaches a maximum at the so-called yellowing point⁵ at which the reaction mixture shows yellow coloration. (3) The third step includes the decomposition of the formed formose sugars under the reaction conditions. Such a complexity, especially the nonselective sugar formation (see Figure 1a), has made detailed analysis of the formose reaction very labor-

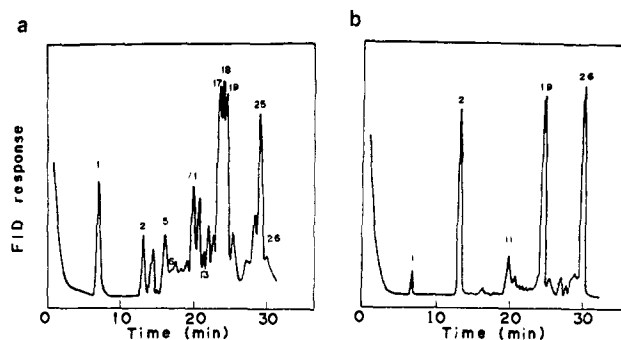


Figure 1. The GLC patterns of trimethylsilylated products obtained from (a) the usual calcium hydroxide catalyzed formose reaction starting from $[HCHO] = 2.0$ M and $[Ca(OH)_2] = 0.22$ M at $60^\circ C$,^{10,11} and (b) the selective formose reaction starting from $[HCHO] = 1.0$ M and $[Ca(OH)_2] = 0.1$ M at $60^\circ C$ followed by removing calcium ions by the addition of oxalic acid at the end of the induction period.

ious, although kinetic approaches were recently done by Weiss et al.⁶⁻⁸

We have developed a method for analyzing the reaction course by measuring the oxidation-reduction potential (ORP) changes during the reaction, which can clearly discriminate each step by an ORP minimum (T_{min}) and maximum (T_{max}) appearing at the end of the induction period and near the yellowing point, respectively.⁹⁻¹² In continuation of our kinetic studies, it was discovered that a number of sugar alcohols are formed with a high selectivity when most of the dissolved calcium ions are removed at T_{min} .

In a typical run, the reaction was started with 1.0 M aqueous formaldehyde solution in the presence of calcium hydroxide (0.1 M) at $60^\circ C$. The progress of the reaction was followed by the ORP measurement. At T_{min} (the time that the induction period is terminated) an equivalent amount of oxalic acid (0.1 M) was added to precipitate the dissolved calcium ions as oxalates. After adjusting the pH to 12.0 with an aqueous potassium hydroxide and the temperature to $60^\circ C$, formose formation occurred, though at a slower rate than that under the usual conditions. At T_{max} (the time that the sugar yield becomes maximum), the reaction was stopped by acidifying the mixture, which was then analyzed for total sugar (24%)¹³ and product distribution was determined by GLC of trimethylsilylated products. The GLC pattern shown in Figure 1b indicated dramatic selective formation of products corresponding to peaks 2, 19, and 26.¹⁴

Addition of potassium dihydrogen phosphate or a calcium-chelating agent such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) at T_{min} was also found to cause the similar selectivity.¹⁵ In these cases, the total GLC peak percent of peaks 2, 19, and 26 amounted to 50-67%. However, addition of sulfuric acid and formic acid in a similar manner resulted in the usual nonselective formose formation. Based on a comparison of solubilities of calcium sulfate (3.4×10^{-2} mol L^{-1}) and calcium formate (5.2×10^{-2}) with those of calcium oxalate (5.2×10^{-4}) and potassium calcium phosphate (1.0×10^{-4}) and also with stability constants of calcium-EDTA (1.2×10^{-6}) and -NTA (1.66×10^{-4}) complexes,¹⁶ it is suggested that the effective concentration of the dissolved calcium ions should be lower than 10^{-3} mol L^{-1} for causing the selective formose reaction.

It was also found that the removal of calcium ions with oxalic acid followed by addition of a certain metal salt such as $Mg(OH)_2$, $Fe(OH)_3$, FeO , and Al_2O_3 (0.1 M) resulted in the similar selective reaction with an increase of the total sugar yield (32-46%) and the total GLC peak percent of peaks 2, 19, and 26 (65-89%),¹⁷ but that addition of barium hydroxide resulted in nonselective formose formation.¹⁸

Products corresponding to GLC peaks 2, 19, and 26 were