Communications to the Editor

Gas-Phase Anionic Oligomerization of Thiacyclopropane Initiated by Allyl Anion

We wish to report the first study of an anion-initiated ring-opening oligomerization reaction in the gas phase where solvent and counterion effects are absent. The monomer is thiacyclopropane and the initiator anion is allyl anion ($C_3H_5^-$). From this study (a) the sequential formation of monomeric through tetrameric anionic oligomers was observed and (b) the rate constants of the initiation and propagation steps leading to $C_3H_5(-CH_2CH_2S-)_3CH_2CH_2S^-$ were determined.

A flowing afterglow (FA) apparatus was used to study this gas-phase oligomerization process at 298 K.[1] Ions are produced in the upstream end of the flow tube by electron impact methods and neutral molecules are added to the flow via inlet ports downstream of the ion production region. A fast flow of helium (P_{He} = 0.5–1.2 torr, flow velocity ($\bar{v}$) = 36–80 m s^{-1}) in the flow tube was the buffer or bath gas in the FA experiments, which served as a third-body in collisional stabilization of vibrationally excited product ions formed in these ion–molecule reactions. The ion composition of the flow was monitored with a quadrupole mass spectrometer. Reaction kinetics were determined under pseudo-first-order conditions where the neutral molecule concentration [N] was much greater than that of the ion concentration. From the slope of the plot of decay of log [ion signal] vs. varying [N] added to the flow, the bimolecular rate constant for the ion–molecule reaction was calculated by methods previously described.[1]

The initiator anion, $C_3H_5^-$, was prepared in the upstream end of the flow tube by the fast (7.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) H^+-transfer reaction between H_2N^- and propene.[2] The vibrationally excited $C_3H_5^-$ ions are cooled to their ground state by numerous collisions (10^3–10^4) with the buffer gas prior to reaching the downstream inlet port where thiacyclopropane was added. The ion–molecule reactions occur in the final 60 cm of the flow tube prior to sampling and analysis using the quadrupole mass spectrometer. Figure 1 is the plot of the percent ion signal vs. concentration of ethylene sulfide added to the flow for the reaction of $C_3H_5^-$ with thiacyclopropane at P_{He} = 1.1 torr and $\bar{v}$ = 36 m s^{-1}. The pseudo-first-order decay of the initiator ions $C_3H_5^-$ and the sequential production of the oligomeric anions *m/z* 101, 161, and 221 are seen. Increasing the concentration of thiacyclopropane beyond that shown in Figure 1 allowed us to observe the slow formation of the tetrameric anion species, *m/z* 281. Formation of the secondary product ion HS^- (*m/z* 33) was also observed as well as its initiation step in yielding ion *m/z* 93.

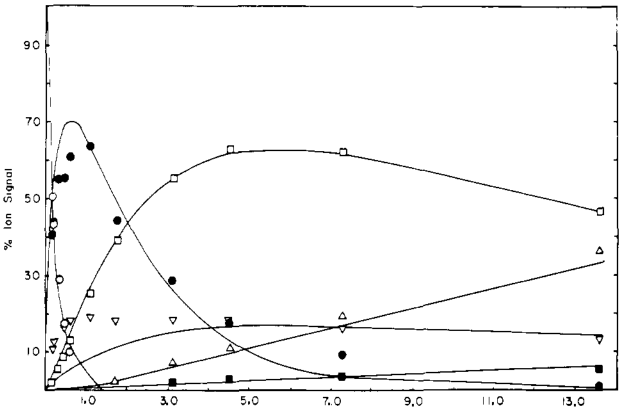


Figure 1. Plot of percent ion signal for the decay of $C_3H_5^-$ (*m/z* 41, ○) and formation of the oligomeric anions *m/z* 101 (●), 161 (□), and 221 (△), the byproduct ion *m/z* 33 (▽), and its oligomerized anion *m/z* 93 (■) for the reaction of $C_3H_5^-$ with $(CH_2)_2S$ vs. added thiacyclopropane. The symbols are data points and the solid lines are the computer-calculated curves for the mechanism and rate constants given in Table I.

The rate constant for the decay of $C_3H_5^-$ was determined to be $(4.0 \pm 0.4) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and was independent of P_{He} (from 0.5 to 1.1 torr, $\bar{v}$ = 80 m s^{-1}). Computer simulation of the data in Figure 1 gave a better fit for the decay of $C_3H_5^-$ with a rate constant of 3×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, which is within the ±30% error considered for FA rate constants. Computer fitting of the remaining data points yielded the calculated curves (solid lines) in Figure 1 using the rate constants for the propagation steps given in eq 2–6 (Table I). In general, the calculated fit of the data is good, although the maximum for monomeric ion *m/z* 101 was missed slightly. The discrepancies in the early part of the fit of the HS^- data are due to O_2 contamination in the propylene. This yields $O_2^-\cdot$ (fast electron transfer from $C_3H_5^-$ to O_2), which produces exclusively HS^- in its fast reaction with thiacyclopropane. This would be important only in the early stages of the reaction until the initiator is consumed, which is the region of Figure 1 where the fit of this ion is poor. Another possibility would be a small amount of H_2S in the thiacyclopropane.

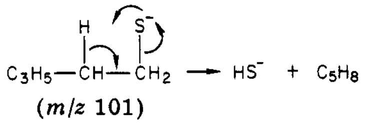
The rate constants for the initiation and propagation steps given in eq 1–4 cover a range of 300. These rate constants are much larger than bimolecular rate constants usually observed in the condensed phase since ion and neutral solvation effects are absent in the present experiment, as are the effects of the counterion.[5] We note that the *intrinsic propagation reactivity* in this oligomerization *decreases* by a factor of 40 from formation of the dimeric species to that for formation of the tetrameric anion species. The absence of constancy in the rate constants for these anionic propagation steps is probably due to the increased polarizability of the increasing oligomer chain and potential ion–dipole and ion–induced dipole interactions between the $-S^-$ growing end with the dipolar $-CH_2-S-CH_2-$ units of the oligomer chains.

As shown in eq 5, formation of the secondary ion HS^- (*m/z* 33) is considered to arise by the unimolecular decomposition of the monomeric ion *m/z* 101. This pathway for formation of HS^- is substantiated from the observation that ions *m/z* 33 and 101 were formed in nearly equal amounts when P_{He} was reduced to 0.5 torr. One mechanism by which HS^- could be formed from *m/z* 101 is shown in eq 7. This unusual form of an intramolecular β-elimination reaction is 14 kcal mol^{-1} endoergic. However, we must recall that ion *m/z* 101 is produced in a reaction that has $\Delta H°$ = −55 kcal mol^{-1}. Therefore, while some of the *m/z* 101 ions are collisionally stabilized by the buffer gas, a fraction of these energetic ions suffer intramolecular fragmentation, releasing HS^-. The mechanism suggested

0024-9297/82/2215-1640$01.25/0

Table I

reaction	k_{calcd}, cm^3 molecule^{-1} s^{-1}	$\Delta H°$, kcal mol^{-1}
$C_3H_5^- + (CH_2)_2S \rightarrow C_3H_5\text{—}CH_2CH_2S^-$ (1) (*m/z* 41) (*m/z* 101)	3 × 10^{-10}	-55.3[3a]
m/z 101 + $(CH_2)_2S \rightarrow C_3H_5\text{—}CH_2CH_2S\text{—}CH_2CH_2S^-$ (2) (*m/z* 161)	4 × 10^{-11}	~ -23[3b]
m/z 161 + $(CH_2)_2S \rightarrow C_3H_5(CH_2CH_2S)_2CH_2CH_2S^-$ (3) (*m/z* 221)	5 × 10^{-12}	~ -23[3b]
m/z 221 + $(CH_2)_2S \rightarrow C_3H_5(CH_2CH_2S)_3CH_2CH_2S^-$ (4) (*m/z* 281)	1 × 10^{-12}	~ -23[3b]
m/z 101 $\rightarrow HS^- + (H_2C{=}CH)_2CH_2$ (5) (*m/z* 33)	1 × 10^{-11}	$+13.9$[3a,c]
m/z 33 + $(CH_2)_2S \rightarrow HSCH_2CH_2S^-$ (6) (*m/z* 93)	3 × 10^{-11}	



(7)

in eq 7 is supported by the fact that HS^- is the exclusive product from the reaction of $O_2^-\cdot$ or F_3C^- with thiacyclopropane where only those protons in the thiacyclopropane molecule could be involved.[7]

The above results and those recently reported for the anionic oligomerization of acrylonitrile[8] demonstrate the potential utility of gas-phase methods to determine various factors associated with the early stages in ionic polymerization reactions in the absence of solvent and counterion effects.

Acknowledgment. We gratefully acknowledge support of this research from the U.S. Army Research Office and the National Science Foundation (equipment grant).

References and Notes

(1) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.

(2) Amide ion was produced by dissociative electron attachment to NH_3 at the electron gun.

(3) (a) $\Delta H_f°(C_3H_5^-)$ = 28.5 kcal mol^{-1};[4a] $\Delta H_f°((CH_2)_2S)$ = 19.7 kcal mol^{-1};[4b] $\Delta H_f°(H_2C{=}CH(CH_2)_3S^-)$ = -7.1 kcal mol^{-1} (calcd)[4c] assuming $\Delta H°_{acid}(H_2C{=}CH(CH_2)_3SH)$ = 356 kcal mol^{-1}.[4a] (b) Modeled by the reaction $CH_3S^- + (CH_2)_2S \rightarrow CH_3S(CH_2)_2S^-$, $\Delta H°$ = -22.6 kcal mol^{-1}; $\Delta H_f°(CH_3S^-)$ = -13.7 kcal mol^{-1};[4a] $\Delta H_f°(CH_3S(CH_2)_2S^-)$ = -16.6 kcal mol^{-1} (calcd)[4c] assuming $\Delta H°_{acid}(CH_3S(CH_2)SH)$ = 356 kcal mol^{-1}.[4a] (c) $\Delta H_f°(HS^-)$ = -18.5 kcal mol^{-1};[4a] $\Delta H_f°((H_2C{=}CH)_2CH_2)$ = 25.3 kcal mol^{-1}.[4b]

(4) (a) Bartmess, J. E.; McIver, R. T. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11. (b) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (c) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(5) To convert the present rate constants (cm^3 molecule^{-1} s^{-1}) to L M^{-1} s^{-1}, multiply the *k*'s by 6 × 10^{20} molecules L M^{-1} cm^{-3}. The collision rate limit for the reaction of $C_3H_5^-$ with $(CH_2)_2S$ is 2.1 × 10^{-9} cm^3 molecule^{-1} s^{-1}, calculated from average dipole orientation theory[6] for gas-phase ion-molecule reactions.

(6) Su, T.; Bowers, M. T. *J. Chem. Phys.* **1973**, *58*, 3027. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 374.

(7) Formation of HS^- is a major product channel in the ion-molecule reactions of H_2N^- and HO^- with COS (DePuy, C. H.; Bierbaum, V. M. *Tetrahedron Lett.* 1981, *22*, 5129), where the intermediate formed by nucleophilic addition to the C=S group could fragment in an analogous manner to eq 7, giving HS^- and the neutrals HNCO and CO_2, respectively.

(8) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 2675.

Richard N. McDonald* and A. Kasem Chowdhury

Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

Received June 1, 1982