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Gas-Phase Anionic Oligomerization of Methyl Acrylate Initiated by F_3C^-, $NCCH_2^-$, and Allyl Anions

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Abstract: The gas-phase anionic oligomerization processes of methyl acrylate initiated by F_3C^-, $NCCH_2^-$, and allyl anion ($C_3H_5^-$) are reported. With F_3C^- (*m/z* 69) as initiator, the oligomerization proceeded by the pseudo-first-order sequence *m/z* 69 → 155 → 241 → 327, with each step involving a $H_2C{=}CHCO_2CH_3$ molecule. One-third of the trimeric anion molecules, *m/z* 327, lost a CH_3OH molecule to yield the anion *m/z* 295. Neither *m/z* 327 nor 295 reacted further with $H_2C{=}CHCO_2CH_3$; thus, the oligomerization was terminated at this point. Through a series of rationalizations and experimental results, it was concluded that the oligomeric anions *m/z* 155, 241, and 327 were the products formed exclusively by 1,4-addition (Michael) of the precursor anion (F_3C^- or an oligomeric enolate anion) with $H_2C{=}CHCO_2CH_3$. Termination of the process occurred by two competitive intramolecular reactions of the trimeric anion *m/z* 327: (1) Dieckmann cyclization and loss of CH_3OH to give *m/z* 295, and (2) H^+ transfer to yield the isomeric, unreactive *m/z* 327 anion, $F_3CCH_2C({=}C(O^-)OCH_3)CH_2CH(CO_2CH_3)CH_2CH_2CO_2CH_3$ (**6**), actually observed. With $C_3H_5^-$ (*m/z* 41) as the initiator anion, the major process was the sequential production of the oligomeric anions *m/z* 127, 213, and 299, with termination occurring primarily by Dieckmann cyclization and loss of CH_3OH to give *m/z* 267, and a minor amount of intramolecular H^+ transfer yielding an isomeric *m/z* 299 anion. In addition to the oligomerization process, formation of *m/z* 71 ($H_2C{=}CHCO_2^-$) was attributed to S_N2 displacement at CH_3 of the ester, and formation of an anion *m/z* 95 and a low steady-state concentration of the initiator anion ($C_3H_5^-$) was observed even at addition of large concentrations of $H_2C{=}CHCO_2CH_3$. These latter two features were explained as the result of some reversible 1,2-addition by $C_3H_5^-$ to the carbonyl group of $H_2C{=}CHCO_2CH_3$. Part of the 1,2-addition adduct loses CH_3OH to give *m/z* 95 ($H_2C{=}CHC(O^-){=}CHCH{=}CH_2$) while most of the adduct reverses to give $C_3H_5^-$ and the vinyl monomer. With $NCCH_2^-$ (*m/z* 40) as initiator, the sequentially formed oligomeric anions were *m/z* 126, 212, and 298. The trimeric anion exhibited a 2:1 preference for Dieckmann cyclization and loss of CH_3OH to give *m/z* 266 vs. H^+ transfer yielding the isomeric anion (*m/z* 298)′ ($NC(CH_2)_2C({=}C(O^-)OCH_3)CH_2CH(CO_2CH_3)(CH_2)_2CO_2CH_3$) (**26**). In this case, **26** undergoes a minor amount of reaction with $H_2C{=}CHCO_2CH_3$, producing the tetrameric anion *m/z* 352 + CH_3OH. In addition, a minor amount of 1,2-addition occurred, producing *m/z* 94 ($H_2C{=}CHC(O^-){=}CHCN$), and an anion *m/z* 180 was formed, the result of intramolecular H^+ transfer in the dimeric anion *m/z* 212 followed by Dieckmann cyclization and loss of CH_3OH. In each of the three oligomerization reactions, the data were computer fitted to obtain rate constants for the individual propagation steps.

Interest in anionic polymerization processes continues to be strong as evidenced by the recent symposium on this topic sponsored by the Division of Polymer Science at the 179th Meeting of the American Chemical Society in March, 1980.[1] Kinetics of anionic polymerizations of vinyl monomers have been examined in polar and nonpolar media.[2] In polar media (e.g., ethers and amines) the kinetics of propagation generally show a fractional dependency on the concentration of growing chains (0.5–1.0). This is explained by assuming that the monomer molecule can react with both the free anion and the anion–cation ion pair of the growing oligomers, but at different rates. Therefore, the ionization constant for ionic dissociation must be known or determined. As might be expected, the propagation rate constants involving the free anion group are several orders of magnitude greater than those of the ion-paired chain ends in those polymerization reactions reported.[2] Kinetic studies of anionic polymerization reactions in nonpolar media (hydrocarbons) are complicated since intermolecular association of the chain ends becomes important; generally organolithium reagents are used as initiators for solubility reasons.[2] The propagation rate constants so determined are average values over rather large molecular weight species.

We wish to report the results of fairly extensive gas-phase ion–molecule studies of the anionically initiated oligomerization of methyl acrylate. In these gas-phase investigations the effects due to solvent (exception: the present experiments are carried out in a buffer gas (He) and collisional stabilization is possible) and counterions are absent. Thus, the intrinsic reactivities of the initiation, propagation, and (possibly) termination steps can be determined. However, such benefits must be weighed against the disadvantage of not being able to isolate and traditionally characterize the various oligomeric products. As we will see in this and future publications in this research area, this disadvantage can usually be overcome. From this gas-phase study: (a) formation and further reaction of the separate oligomeric anions $R(CH_2CH(CO_2CH_3))_n^-$ (n = 1–3, R^- is the initiator anion) are directly observed, (b) the rate constant for each step is obtained, and (c) the last observed oligomeric anion (n = 3) terminates the anion chain reaction by competitive intramolecular H^+ transfer to produce a new, stabilized enolate anion and Dieckmann cyclization followed by loss of a CH_3OH molecule to yield the conjugate base of the cyclized β-keto ester.

Experimental Section

The gas-phase technique used in the studies involves the flowing afterglow (FA) apparatus previously described[3] with certain modifications. The present system uses a water-cooled Varian chevron baffle to separate the 6-in. diffusion pump and the analysis section and a Pfeiffer 500 L s^{-1} turbomolecular pump backed by a mechanical pump to maintain the 10^{-7}-torr pressure in the quadrupole mass spectrometer compartment.[3] The 1.5 m × 7.15 cm i.d. stainless steel flow tube is of a modular design, which allows introduction of neutral gas inlets and spacers as needed to fit the requirements of the experiment. All pressures for gas loading and dispensing of gases as well as the flow tube pressure are measured directly by using Baratron capacitance monometers. The modified FA apparatus is shown in Figure 1.

Briefly, H_2N^- was produced by dissociative electron attachment with NH_3, the latter being mixed with the helium buffer gas and flowed past the electron gun. In separate experiments, the primary initiator anions (F_3C^-, $NCCH_2^-$, and $C_3H_5^-$) were produced when their conjugate acids were added to the helium flow containing H_2N^- through a port located just downstream of the electron gun (Figure 1) and fast H^+-transfer reactions occurred. These initiator anions were formed vibrationally excited and were cooled to their ground states by numerous collisions with the helium buffer gas prior to reaching the neutral inlet port of $H_2C{=}CHCO_2CH_3$ located 45 cm downstream of the electron gun. The ion–

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(1) *ACS. Symp. Ser.*, **1981**, *No. 166*.

(2) Morton, M., Chapter 2 in ref 1.

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

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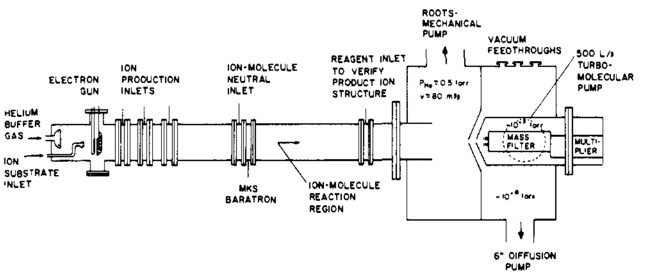

Figure 1. Diagram of the flowing afterglow apparatus.

molecule reaction distance (neutral inlet port to first sampling nose cone[3]) was 62.5 cm.

Helium was the buffer gas and was inletted into the upstream end of the flow tube. The buffer gas pressure (P_{He}) and flow velocity ($\bar{v}$) were maintained by a Stokes Roots blower/mechanical pump system (Model 1722-S). These two parameters could be varied from P_{He} = 0.2 to 1.2 torr and $\bar{v}$ = 36 to 80 m s^{-1} by throttling a gate valve and/or altering the helium inlet flow. In these oligomerization studies, the standard operating conditions were P_{He} = 1.1 torr and $\bar{v}$ = 36 m s^{-1} at 298 K. Rate constants for the initiation and first propagation steps were also determined at P_{He} = 0.5 torr and $\bar{v}$ = 80 m s^{-1} to see if a P_{He} dependency was present; none was observed in these experiments.

The helium used in this study was of 99.99% purity supplied by Welders Products and was further purified by passage through two traps filled with Davison 4-Å molecular sieves cooled with liquid nitrogen and then warmed to room temperature in a glass coil prior to introduction into the flow tube. Gas and liquid reagents were obtained from commercial sources ($H_2C{=}CHCO_2CH_3$, Eastman; CH_3CN, Fisher; F_3CH and $CH_3CH{=}CH_2$, Matheson). The liquid reagents were distilled just prior to use and a center-cut, constant-boiling-point sample was transferred to a gas storage bulb after three freeze–pump–thaw degassing cycles. The gas reagents were used directly.

Results and Discussion

Oligomerization of $H_2C{=}CHCO_2CH_3$ Initiated by F_3C^-. The initiator anion F_3C^- (*m/z* 69) was produced in the upstream end of the flow tube by the fast ion–molecule reaction (H^+ transfer) of H_2N^- with F_3CH ($k = (1.3 \pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}). Addition of $H_2C{=}CHCO_2CH_3$ via the neutral inlet port downstream of the ion preparation/thermalization region (Figure 1) to the flow containing F_3C^- (flow conditions: P_{He} = 0.45 torr, $\bar{v}$ = 80 m s^{-1}) produced the adduct *m/z* 155 along with lesser amounts of the oligomeric anions *m/z* 241 and 327 (trace). From the decay of *m/z* 69 in a plot of log *m/z* 69 signal vs. the concentration of added $H_2C{=}CHCO_2CH_3$, the rate constant, $k = (1.5 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, for the bimolecular reaction of $F_3C^- + H_2C{=}CHCO_2CH_3 \rightarrow m/z\ 155$ was calculated.[3]

Formation of the higher molecular weight anions *m/z* 241 and 327 appeared to follow the pseudo-first-order sequence of reactions *m/z* 69 → 155 → 241 → 327 ($\delta m/z$ 86), with each step involving a $H_2C{=}CHCO_2CH_3$ molecule. Since we will establish shortly that the trimeric anion *m/z* 327 loses CH_3OH to yield an anion *m/z* 295, each of these oligomeric anions (*m/z* 155, 241, and 327) must be covalently bound structures rather than being loose, ion–dipole complexes.

The flow outlet gate valve[3] was partially throttled to allow observation of the full course of this oligomerization reaction, which increased the pressure (P_{He} = 1.1 torr) and reduced the velocity ($\bar{v}$ = 36 m s^{-1}) of the flow in this experiment. This change in $\bar{v}$ from 80 to 36 m s^{-1} increased the ion–molecule reaction time from ~7.5 to ~16.7 ms, respectively, in the 62.5-cm-long reaction region of the flow tube. We assume that the same parabolic flow parameters apply to both sets of flow conditions.[3] The semilog plot of ion signal vs. concentration of $H_2C{=}CHCO_2CH_3$ added to the flow initially containing F_3C^- under these conditions is shown in Figure 2.

The data in Figure 2 clearly demonstrate the pseudo-first-order decay of the signal for F_3C^- as a function of $H_2C{=}CHCO_2CH_3$. The bimolecular rate constant for this reaction under these conditions was the same as that determined at P_{He} = 0.45 torr, $\bar{v}$ = 80 m s^{-1} (above). As expected, the sequential production of the anions *m/z* 155, 241, and 327 was now clearly established (see above), and 29% of the *m/z* 327 ions undergo loss of CH_3OH to yield the *m/z* 295 anion (eq 1–4). It was clear from this data

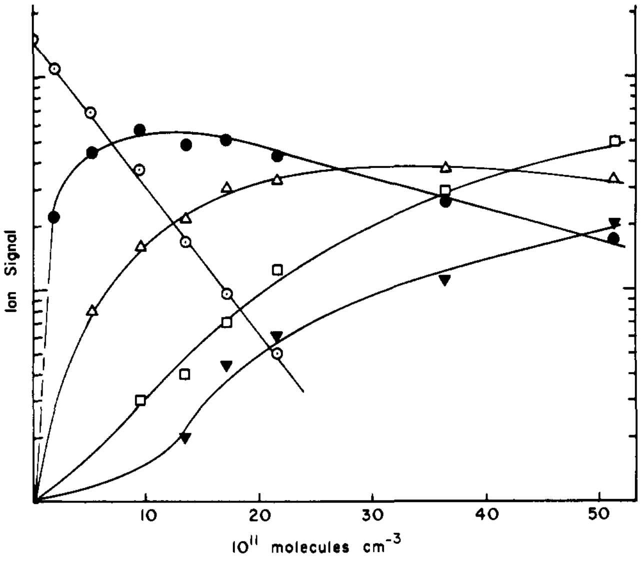

Figure 2. Semilog plot of the decay of F_3C^- (*m/z* 69, ⊙) and formation of product anions (*m/z* 155, ●; *m/z* 241, △; *m/z* 327, □; *m/z* 295, ▼) for the reaction of $F_3C^- + H_2C{=}CHCO_2CH_3$; P_{He} = 1.1 torr, $\bar{v}$ = 36 m s^{-1}. Ion signals are in arbitrary units and are uncorrected for mass discrimination.

$$\underset{m/z\ 69}{F_3C^-} + H_2C{=}CHCO_2CH_3 \rightarrow m/z\ 155 \qquad (1)$$

$$m/z\ 155 + H_2C{=}CHCO_2CH_3 \rightarrow m/z\ 241 \qquad (2)$$

$$m/z\ 241 + H_2C{=}CHCO_2CH_3 \rightarrow m/z\ 327 \qquad (3)$$

$$m/z\ 327 \rightarrow m/z\ 295 + CH_3OH \qquad (4)$$

that termination of the oligomerization process had occurred at the trimeric stage in that no higher molecular weight oligomers were observed from anions *m/z* 327 and 295.[4] While these data resemble the sequential clustering of anions by weakly acidic molecules,[5] the fact that CH_3OH was eliminated from the trimeric anion, *m/z* 327, requires that this ion (and its precursor ions) be covalently bonded.

When we begin the task of attempting to assign structures to the oligomeric anions *m/z* 155, 241, and 327, a structural tree unfolds (Scheme I). The only constraints we placed on the oligomerization process was (a) that nucleophilic additions to $H_2C{=}CHCO_2CH_3$ occurred either by 1,2-[6] or 1,4-addition (Michael) mechanisms,[6a,7] and (b) that the enolate anions produced by nucleophilic 1,4-addition reactions could behave as ambident nucleophiles in the next step, reacting either at C_α or O.[8] Thus, the structural tree contains 2 possibilities for *m/z* 155, 6 possibilities for *m/z* 241, and 18 possible structures for the trimeric *m/z* 327 anion.

The two possible structures of the adduct *m/z* 155 are the conjugate base of the hemiketal **1** formed by 1,2-addition and the

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(4) Assuming that the rate constants for the reactions of *m/z* 327 or 295 with $H_2C{=}CHCO_2CH_3$ were only 10% of that for the reaction *m/z* 241 + $H_2C{=}CHCO_2CH_3$ (see text), formation of the tetrameric species *m/z* 413 or 381 would have been readily observed. The upper limit of the mass range of the quadrupole mass spectrometer is ~500 amu.

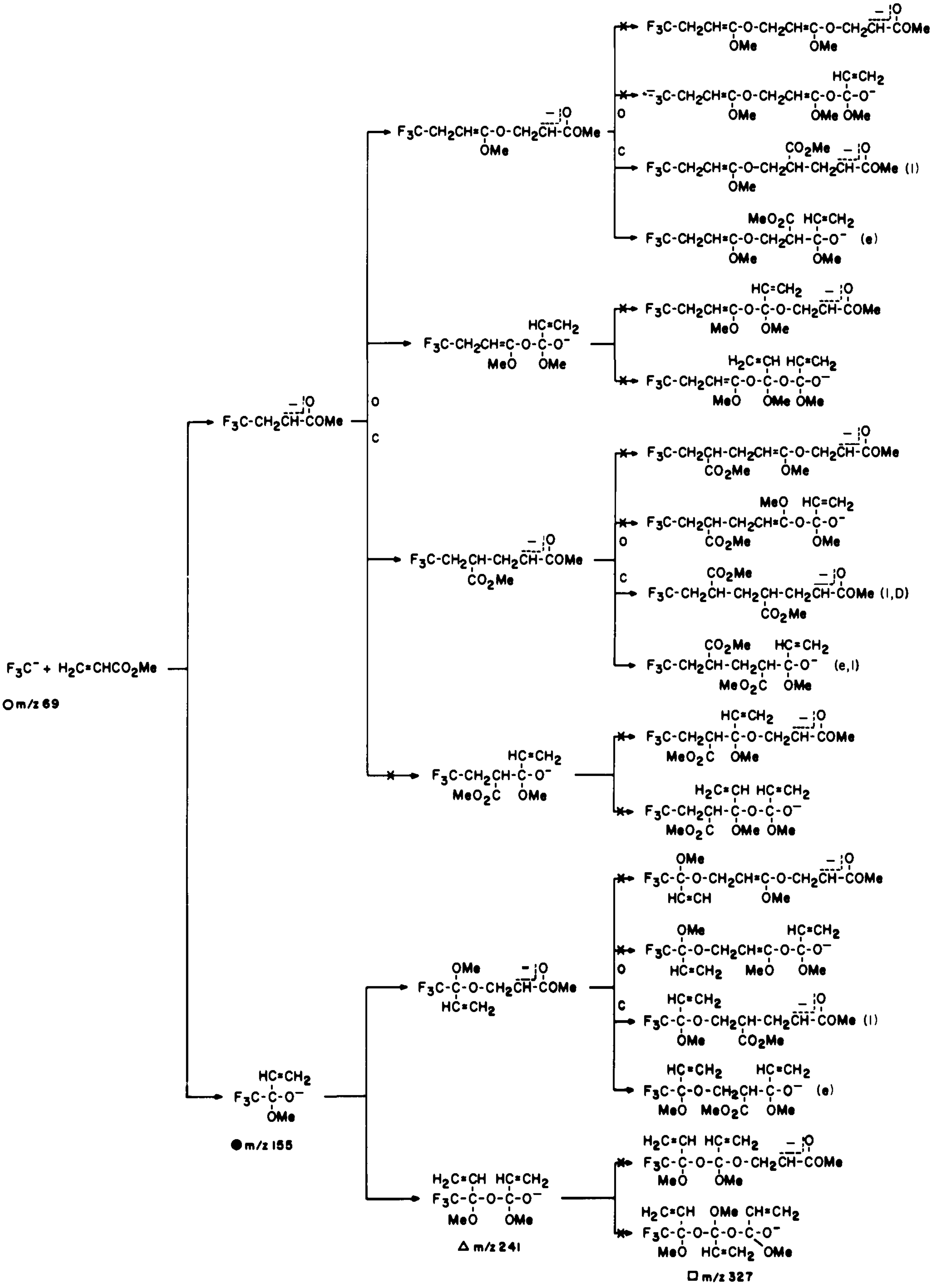
(5) (a) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 6599, 7586. (b) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

(6) (a) McDonald, R. N.; Chowdhury, A. K. *J. Phys. Chem.* **1982**, *86*, 3641. (b) *J. Am. Chem. Soc.* **1980**, *102*, 6146.

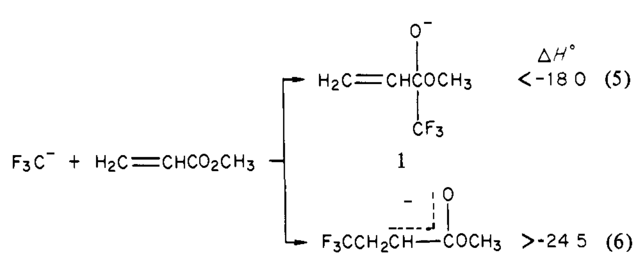
(7) (a) Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76 and references therein. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7586.

(8) Bartmess et al. (Bartmess, J. E.; Hays, R. L.; Caldwell, G. *J. Am. Chem. Soc.* **1981**, *103*, 1338) conclude that O^- of an enolate anion is not involved as a nucleophilic center in certain gas-phase Claisen condensation reactions.

Scheme I



enolate anion **2** produced by 1,4-addition (eq 5 and 6, $\Delta H°$ values are in kcal mol^{-1}). Even with favorable assumptions about the stability of **1** compared to that of **2**,[9,12] eq 6 is the more exothermic reaction channel. Of the six structures for the dimeric species *m/z* 241, given in Scheme I, one of them, **3**, can be eliminated. Anion **3** is the product of an exothermic ($\leq$-20 kcal mol^{-1}) Claisen condensation reaction and should readily lose CH_3OH to yield an anion *m/z* 209, the enolate anion of the resultant β-keto ester;[8] this was not observed. We, further, remove from consideration the two trimeric anion structures derived from **3**.



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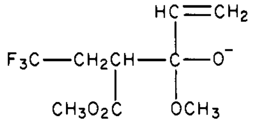

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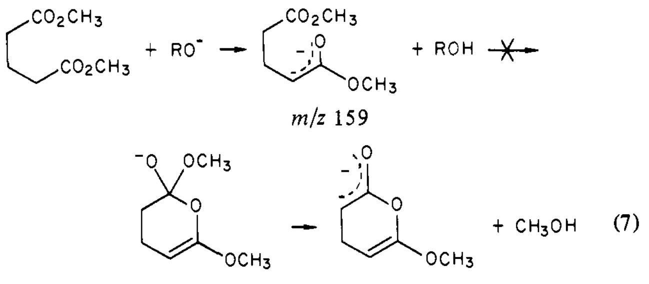
Ten of the remaining 16 possible structures of the trimeric anion *m/z* 327 in Scheme I have X's marked through the arrows producing them. These 10 trimeric structures do *not* allow for loss of CH_3OH by any reasonable mechanism to produce a corresponding *m/z* 295 ion where the parent and/or daughter anions would not be expected to react further with $H_2C{=}CHCO_2CH_3$. Therefore, these 10 structures cannot lead to the observed termination of the telomerization process and cannot represent the trimeric anion *m/z* 327.

Of the remaining six possible trimeric structures, they are classified by letters in parentheses following the structure: three structures are marked with an e, four are marked with an l, and a single structure is followed by a D. The symbol e refers to those structures that should readily eliminate CH_3OH to produce the stable and unreactive conjugate base of the corresponding β-keto ester.[8] These structures could satisfy the requirement for termination of the process at this stage. However, since these structures of the *m/z* 327 and their corresponding *m/z* 295 ions have a parent–daughter relationship *and both are observed*, the ratio of these two ions should change as the number of stabilizing collisions with the helium buffer gas is changed. Experimentally, it was found that the ratio of the ions (*m/z* 327)/(*m/z* 295) remained constant as the helium flow pressure was varied from 0.5 to 1.2 torr. Therefore, we remove the e-marked structures as important contributors to the trimeric *m/z* 327 ions.

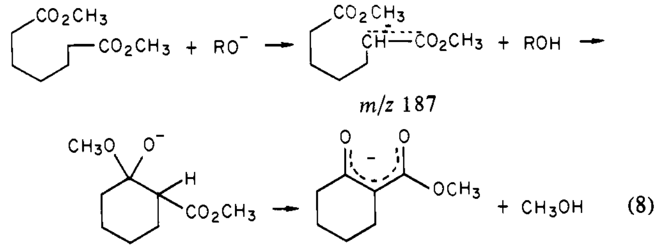
We are left with the four structures classified with an l and the single structure marked with a D for the trimeric anions in Scheme I. The l refers to the mechanism of lactonization where O^- of the enolate anion would add to the carbonyl carbon (sixth atom from O^-) of an ester group on the backbone with the resulting six-membered ring lactone losing CH_3OH to yield a new enolate anion. The D refers to the Dieckmann cyclization reaction involving the methine carbon of the enolate anion adding to the carbonyl carbon of an ester via a six-membered-ring intermediate followed by loss of CH_3OH to yield the conjugate base of the cyclized β-keto ester.

Both of these mechanistic possibilities have been modeled by using H^+-abstraction reactions from dimethyl glutarate for the lactonization mechanism and dimethyl pimelate for the Dieckmann cyclization mechanism with essentially identical gas-phase results obtained at both high[13] and low pressure.[14] Reaction of an alkoxide anion, RO^-, with dimethyl glutarate yields the ester-enolate anion, *m/z* 159, which shows no tendency to lose CH_3OH (eq 7).[14] Thus, the lactonization mechanism appears unreasonable as the source of *m/z* 295 from *m/z* 327 produced in this telomerization reaction. On the other hand, the reaction of RO^- with dimethyl pimelate proceeded rapidly to yield mainly the ion *m/z* 155 with only ~1% of the product-ion signals due to *m/z* 187, the conjugate base of the diester (eq 8).[14] We conclude that the Dieckmann cyclization is the mechanism by which the trimeric anion *m/z* 327 loses CH_3OH to produce the anion *m/z* 295.



m/z 159

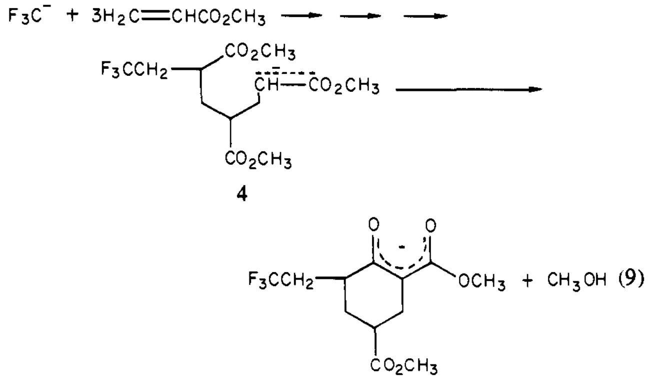
m/z 127



m/z 187

m/z 155

Returning to Scheme I, our results and considerations have reduced the 18 possible structures of the trimeric anion *m/z* 327 to a unique one, **4**. Anion **4** was formed by three successive conjugate, 1,4-addition reactions and loses CH_3OH to give *m/z*



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[9] Using Benson's additivity rules,[10] we calculate $\Delta H_f°$ (**1** conjugate acid) = −235.9 kcal mol^{-1}. If we assume that $\Delta H°_{acid}$ (**1** conjugate acid) is 10 kcal mol^{-1} lower (more acidic) than that of CF_3CH_2OH ($\Delta H°_{acid}$ = 364.4 kcal mol^{-1}),[11] then $\Delta H_f°$ (**1**) = −248.7 kcal mol^{-1} is obtained. $\Delta H_f°(H_2C{=}CHCO_2CH_3)$ = −73.9 kcal mol^{-1} was calculated.[10]

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

[11] Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chap 11.

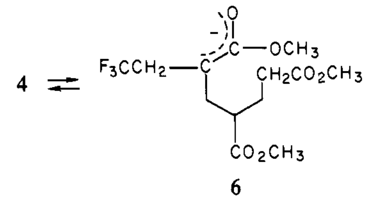
[12] $\Delta H_f°$ ($CF_3CH_2CH_2CO_2CH_3$) = −259.4 kcal mol^{-1} (calcd).[10] If we assume *no* substitutent stabilizing effect by the α-CF_3CH_2 group on the ester enolate anion, then $\Delta H°_{acid}$ ($CF_3CH_2CH_2CO_2CH_3$) = $\Delta H°_{acid}$ ($CH_3CO_2CH_3$) = 371.0 kcal mol^{-1},[11] from which $\Delta H_f°$ ($CF_3CH_2CHCO_2CH_3^-$) = −255.6 kcal mol^{-1} is calculated; this is an upper limit for this enolate anion. $\Delta H_f°$ (CF_3^-) = −157.2 kcal mol^{-1}.[11]

[13] Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953.

[14] Data obtained by R.N.M. in collaboration with Dr. Sahba Ghaderi, Nicolet Analytical Instruments, using the Nicolet FT-MS 1000 at 10^{-7} torr with *n*-BuO$^-$ as base.

295 (**5**) via a Dieckmann cyclization reaction (eq 9). While the proposed transformation of **4** → **5** + CH_3OH is readily understood, structure **4** cannot represent the large amount of "unreactive" anion *m/z* 327 observed in Figure 2 for the following reasons: (a) the results of reaction of RO^- with dimethyl pimelate (eq 8) suggest that ion **4** should completely yield **5** and *m/z* 327 would not be observed and (b) the total termination of the oligomerization at this point requires that **4** is not the structure of the trimeric species *m/z* 327 since if it did not cyclize, it would be expected to continue to react with $H_2C{=}CHCO_2CH_3$ to yield higher oligomers on the basis of the similarity of the structure of **4** and its precursor ions.

To account for this "unreactive" form of the trimeric anion (*not* **4**), we have considered three possibilities. (1) An intramolecular H^+ transfer from **4** to give **6** via a six-membered-ring transition



(10)

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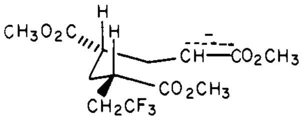
state could be competitive with the intramolecular Dieckmann condensation reaction (eq 9). The proximity of the CF_3 initiator group in **4** to the C–H bond involved in the H^+ transfer would be expected to drive the equilibrium in the direction of **6**. Further, **6** could not undergo a Dieckmann cyclization and loss of CH_3OH as did **4**, and **6** would be stabilized toward further reaction with the monomer, $H_2C{=}CHCO_2CH_3$, due to the field/inductive effects of the CF_3 group and the higher substitution of the enolate anion. (2) Possibly different conformers, e.g., **7** and **8**, of *m/z*



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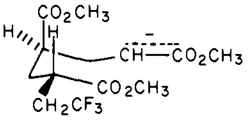

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327 were produced that cyclize at different rates. While this could account for the steady ratio of (*m/z* 327)/(*m/z* 295) = 2 as perhaps the ratio [**8**]/[**7**] since **8** would be expected to be slower to cyclize due to the axial CO_2CH_3 group, **8** should continue the oligomerization process to yield higher molecular weight oligomers. (3) The observed *m/z* 327 ions have one or more of the other 17 trimeric structures originally ruled out in Scheme I. While this is a real possibility, we hoped that nature would not be that cruel.

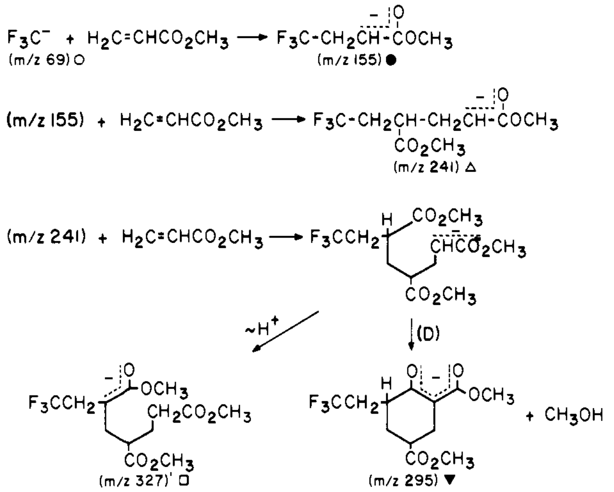
There is an experimental test of possibility (1) above. As pointed out, the presence of the CF_3 group allows the equilibrium of eq 10 to be competitive with the intramolecular Dieckmann cyclization reaction. Therefore, we should observe a change in the ratio of the trimeric anion to that of the (trimer − $CH_3OH)^-$ as the initiator anion is varied. The results of such experiments with $H_2C{=}CHCO_2CH_3$ using F_3C^-, $NCCH_2^-$, and $C_3H_5^-$ as anionic initiators are given in Table I; the data for $NCCH_2^-$- and $C_3H_5^-$-initiated oligomerization reactions are presented in the following sections of this paper. Replacing the CF_3 group in structure **4** with the $NCCH_2$ group should produce less H^+ transfer in competition with Dieckmann cyclization and loss of CH_3OH ((trimer − $CH_3OH)^-$) since the acidifying effect of the cyano group is one more methylene group removed from the C–H bond involved in the H^+ transfer. Indeed, the ratio of (trimer)$^-$/(trimer − $CH_3OH)^-$ decreased from 2 with CF_3^- as the initiator to 0.67 with $NCCH_2^-$ as the initiator anion (Table I). A further large decrease in this ratio to 0.07 was observed by using allyl anion ($C_3H_5^-$) as the initiator anion since we would expect a very limited tendency for H^+ transfer to occur in **4** with the CF_3 group replaced by the allyl group. The Dieckmann cyclization should show no such substitutent effect.

Table I. Ratio of (Trimer)$^-$/(Trimer–$CH_3OH)^-$ Formed in the Anionic Oligomerization of $H_2C{=}CHCO_2CH_3$ as a Function of Initiator Structure

	(trimer)$^-$		(trimer − $CH_3OH)^-$
$F_3C^- + H_2C{=}CHCO_2Me \rightarrow$	2	/	1
$NCCH_2^- + H_2C{=}CHCO_2Me \rightarrow$	1	/	1.5
$C_3H_5^{-a} + H_2C{=}CHCO_2Me \rightarrow$	1	/	15

[a] Allyl anion.

Scheme II



We consider that the results presented above for the effect of changing the initiator anion on the (trimer)$^-$/(trimer − $CH_3OH)^-$ ratio strongly support the proposal that the initially formed trimeric anion **4** undergoes two competitive intramolecular reactions: (a) H^+ transfer giving the isomeric enolate anion **6** and (b) Dieckmann cyclization and loss of CH_3OH yielding enolate anion **5**. These results *do not* agree with expectations concerning the possible involvement of different conformers (e.g., **7** and **8**) where only very minor changes (if any) would be expected in the (trimer)$^-$/(trimer − $CH_3OH)^-$ ratio with such changes in the initiator anion structure. We are unable to comment on possibility (3) above since the complexity involving 1 or more of the 17 other structures in Scheme I is so great. However, we see no obvious way of accommodating the above data with this possibility, and we dismiss it since interpretation of *all* of the experimental results does not require this added complexity.

We now arrive at the mechanism for the CF_3^--initiated gas-phase oligomerization of $H_2C{=}CHCO_2CH_3$ (data in Figure 2) with structural assignments for the oligomeric intermediates and final products shown in Scheme II. This involves a sequence of three conjugate 1,4-addition reactions leading to the trimeric anion *m/z* 327, which undergoes the competitive, intramolecular reactions of H^+ transfer to produce the *observed* (*m/z* 327)′ anion and Dieckmann cyclization followed by loss of CH_3OH to give *m/z* 295, the conjugate base of the cyclized β-keto ester. Use of this mechanism and the experimentally determined rate constant for the initiation step ($F_3C^- + H_2C{=}CHCO_2CH_3 \rightarrow$ *m/z* 155) in a computer simulation of the data in Figure 2 gives an excellent fit, with the rate constants for the two propagation steps of $k_2 = k_3 = 4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The partitioning ratio (0.3/0.7) of *m/z* 327 (**4**) to yield *m/z* 295 (**5**) and (*m/z* 327)′ (**6**) is taken directly from the ion signal intensities of these ions in Figure 2.

Oligomerization of $H_2C{=}CHCO_2CH_3$ Initiated by Allyl Anion. Allyl anion ($C_3H_5^-$, *m/z* 41) was prepared by the fast H^+-transfer reaction ($k = (7.5 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) between H_2N^- and propylene in the ion preparation/thermalization region of the flow tube. Addition of $H_2C{=}CHCO_2CH_3$ via the downstream neutral port to the flow containing $C_3H_5^-$ (flow conditions: P_{He} = 0.5 torr, $\bar{v}$ = 80 m s^{-1}) produced mainly the adduct *m/z* 127 along with lesser amounts of the anions *m/z* 71, 95, 213, and 267. The bimolecular rate constant calculated from the pseudo-first-order decay of log $C_3H_5^-$ ion signal vs. [$H_2C{=}CHC$-

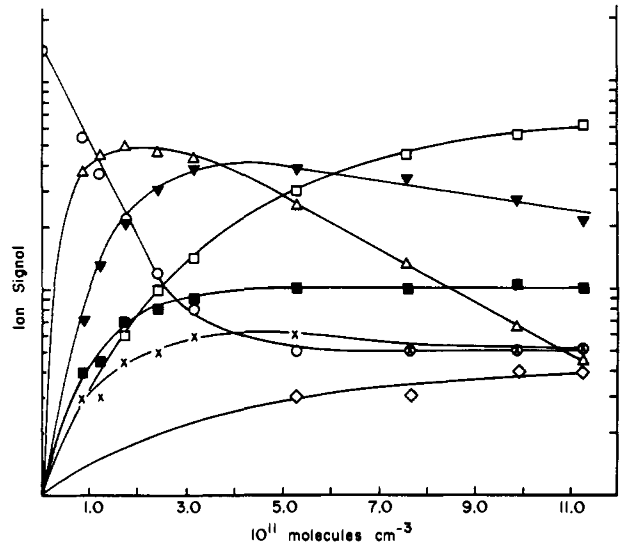


Figure 3. Semilog plot of the decay of $C_3H_5^-$ (*m/z* 41, ○) and formation of product anions (*m/z* 71, ■; *m/z* 95, X; *m/z* 127, △; *m/z* 213, ▼; *m/z* 267, □; *m/z* 299, ◇) for the reaction of $C_3H_5^-$ + $H_2C{=}CHCO_2CH_3$; P_{He} = 1.1 torr, $\bar{v}$ = 36 m s^{-1}. Ion signals are in arbitrary units and are uncorrected for mass discrimination.

Table II. Rate Constants for the S_N2 Reactions of $C_3H_5^-$, CF_3^-, and $NCCH_2^-$ with the Methyl Halides

R	*k*, cm^3 $molecule^{-1}$ s^{-1}	
	CH_3Br	CH_3Cl
$C_3H_5^-$	7.7×10^{-10}	2.9×10^{-10}
CF_3^-	2.8×10^{-10}	5.6×10^{-11}
$NCCH_2^-$	3.6×10^{-10}	2.6×10^{-11}

O_2CH_3] added to the flow was $k = (9.4 \pm 0.6) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. When the flow conditions were changed (P_{He} = 1.1 torr, $\bar{v}$ = 36 m s^{-1}) to enable us to observe the full sequence of reactions of $C_3H_5^-$ with $H_2C{=}CHCO_2CH_3$, the data shown in Figure 3 were obtained.

Several features of Figure 3 are quite similar to those seen and previously discussed in Figure 2, while certain other features of Figures 2 and 3 are strikingly different. The major similar features are (a) the major sequential production of the oligomeric anions *m/z* 127, 213, and 299 ($\delta m/z$ 86), (b) loss of CH_3OH from *m/z* 299 to give *m/z* 267, and (c) termination of the oligomerization process at the trimeric anion *m/z* 299 (and *m/z* 267). Major differences between the data in these two figures are (d) formation of two anions *m/z* 71 and 95 that may or may not be derived from the telomers, (e) the development of a small, steady-state concentration of the initiator anion $C_3H_5^-$ in the presence of high concentrations of the vinyl monomer, and (f) the apparently inverted ratio of (*m/z* 299)/(*m/z* 267) = 0.07, assuming that these product anions are related to the ions *m/z* 327 and 295 from the F_3C^--initiated oligomerization of $H_2C{=}CHCO_2CH_3$ (Figure 2).

Let us deal with the three differences (d–f) first. The probable source of anion *m/z* 71 is an S_N2 displacement reaction of $C_3H_5^-$ on the CH_3 group of $H_2C{=}CHCO_2CH_3$ producing $H_2C{=}CHCO_2^-$. Of the three initiator anions used in this study, $C_3H_5^-$ is the best S_N2 nucleophile in the reactions of these anions with CH_3Br and CH_3Cl (Table II).[15]

The structure and source of anion *m/z* 95 can potentially be coupled with difference e in the following way. We previously demonstrated that $C_3H_5^-$ does undergo 1,2-addition to carbonyl groups of certain esters.[16] If 1,2-addition occurred, at least in part, in the reaction of $C_3H_5^-$ with $H_2C{=}CHCO_2CH_3$, the intermediate adduct anion **10** would be expected to fragment to the collision complex **11** where fast H^+ transfer would yield enolate anion **13**, *m/z* 95, and CH_3OH via collision complex **12** (eq 11).

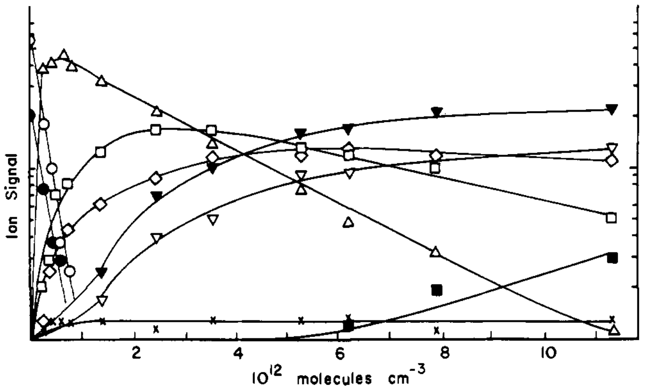
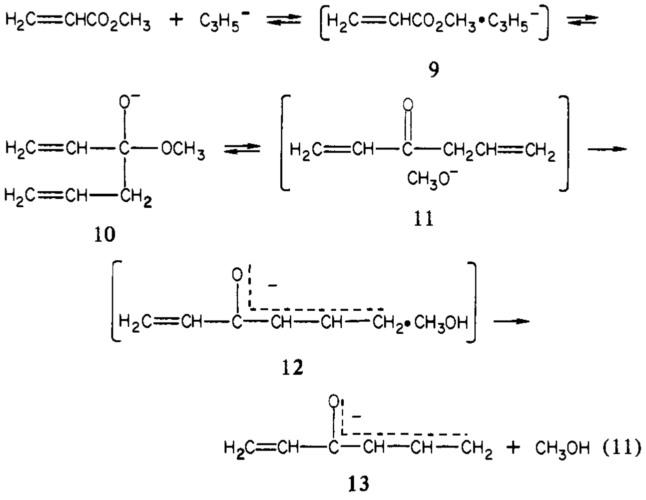


Figure 4. Semilog plot of the decay of $NCCH_2^-$ (*m/z* 40, ○) and $NCCH_2(CH_3CN)$ (*m/z* 81, ●) and formation of product anions (*m/z* 94, X; *m/z* 126, △; *m/z* 180, ◇; *m/z* 212, □; *m/z* 266, ▼; *m/z* 298, ▽; *m/z* 352, ■) for the reaction of $NCCH_2^-$ with $H_2C{=}CHCO_2CH_3$; P_{He} = 1.1 torr, $\bar{v}$ = 36 m s^{-1}. Ion signals are in arbitrary units and are uncorrected for mass discrimination.



(11)

If we assume that the two collision complexes **9** and **11** involve the same ion–dipole and ion-induced dipole attractive forces, fragmentation of intermediate **10** to give **11** is favored by only 4.7 kcal mol^{-1} [10,11] compared to (reverse) fragmentation of **10** to yield **9**. Since the potential energy barriers separating **10** and **11**, and **9** and **10** will "feel" only a fraction of the $\delta\Delta H°$,[17] and therefore be quite similar in magnitude, the 1,2-addition channel of $C_3H_5^-$ to $H_2C{=}CHCO_2CH_3$ is the most reasonable candidate for the small steady-state concentration of $C_3H_5^-$ observed in Figure 3 and is the source of anion *m/z* 95 (**13**).

The above conclusion means that some contribution of anions of structure **10** may be present in the monomeric ions *m/z* 127. If **10** reacts further with $H_2C{=}CHCO_2CH_3$ by 1,2- and/or 1,4-addition, contributions by these oligomeric ion structures (see Scheme I, replacing CF_3 by the 2-propenyl group) are possible in the dimeric (*m/z* 213) and trimeric anions (*m/z* 299). However, we note that of the six trimeric structures so derived from **10**, *all* six would be expected to react further with $H_2C{=}CHCO_2CH_3$, and none of these six structures could loss CH_3OH to yield a daughter ion *m/z* 267 which would be unreactive toward the vinyl monomer. Therefore, the contributions of **10** and the derived higher oligomeric anion structures from **10** are considered minor at best.

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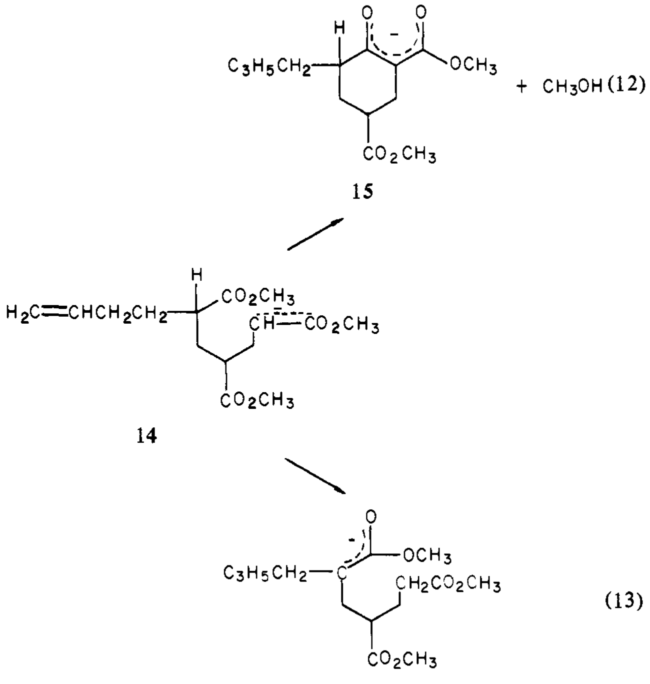
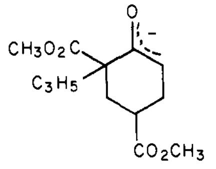
(15) For general presentations of gas-phase S_N2 nucleophilic reactivity, see: Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. Tanaka, K.; MacKay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(16) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 901.

(17) At this point, we are unable to calculate the $\delta\Delta S°$ contribution in these two fragmentation channels from **10**.

As in the F_3C^--initiated oligomerization of $H_2C{=}CHCO_2CH_3$, the structure of the (trimer - $CH_3OH)^-$ anion (**15**) was considered to be uniquely produced by Dieckmann cyclization of trimeric anion **14** followed by loss of CH_3OH (eq 12). To account for the small amount of m/z 299 observed (Figure 3), we propose that intramolecular H^+ transfer occurs to yield the tertiary enolate anion **16** (eq 13) in competition with the Dieckmann reaction (eq 12). Tertiary enolate anion **16** would be unreactive in a Dieckmann cyclization; should this cyclization occur, loss of CH_3OH would yield a simple ketone enolate anion of the cyclized β-keto ester **17**. The small amount of m/z 299 (**16**) observed and the expected reduced reactivity of this tertiary enolate anion structure toward $H_2C{=}CHCO_2CH_3$ would effectively terminate the oligomerization at this point under the present gas-phase reaction conditions. The fact that the ratio $(m/z\ 267)/(m/z\ 299) = 15$ in this oligomerization reaction says that intramolecular H^+ transfer (**14** → **16**) is slow compared to the intramolecular Dieckmann condensation. Farneth and Brauman[18] have shown that slow H^+-transfer reactions were observed in various intermolecular reaction involving closely related delocalized enolate anions.





17

These results and considerations lead to the formulation of the mechanism for the $C_3H_5^-$-initiated oligomerization of $H_2C{=}CHCO_2CH_3$ (data in Figure 3) with structural assignments for the various observed anionic species given in Scheme III. Computer simulation of the data in Figure 3 using the mechanism in Scheme III and the rate constant for the initiation step produced only a fair fit of the data. The equilibrium formation of the 1,2-addition adduct **10** appeared to be a major problem with the simulation. However, similar rate constants for the propagation steps were obtained in this and the F_3C^--initiated oligomerization processes.

Oligomerization of $H_2C{=}CHCO_2CH_3$ Initiated by $NCCH_2^-$. Generation of the initiator anion, $NCCH_2^-$ (m/z 40), was accomplished by the fast H^+-transfer reaction ($k = (4.5 \pm 0.3) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1})[19] of H_2N^- with CH_3CN in the upstream end of the flow tube. Formation of m/z 40 was accompanied by the secondary ion-solvent cluster formation of m/z 81 (eq 14 and 15). When $H_2C{=}CHCO_2CH_3$ was added to the flow containing

$$H_2N^- + CH_3CN \rightarrow \underset{m/z\ 40}{NCCH_2^-} + NH_3 \qquad (14)$$

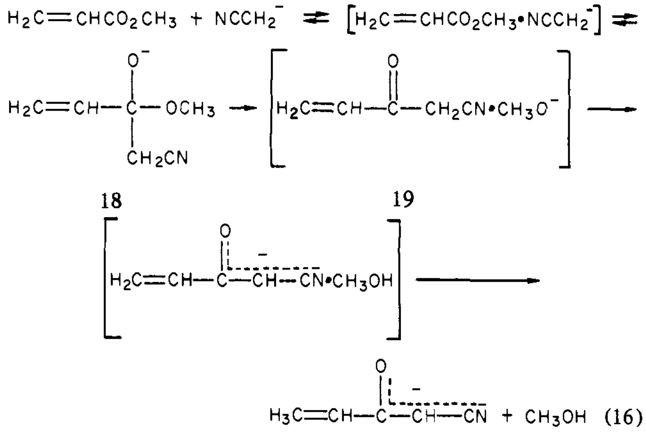
$$NCCH_2^- + CH_3CN \rightarrow \underset{m/z\ 81}{NCCH_2^-(CH_3CN)} \qquad (15)$$

m/z 40 and 81 ($P_{He} = 0.49$ torr, $\bar{v} = 80$ m s^{-1}), the major product ion formed was m/z 126 along with small amounts of anions m/z 94, 180, and 212. The bimolecular rate constants for the decay of m/z 40 and 81 were the same value, $k = (3.7 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. When P_{He} was increased to 1.1 torr and $\bar{v}$ was reduced to 36 m s^{-1}, the full extent of the oligomerization of $H_2C{=}CHCO_2CH_3$ initiated by $NCCH_2^-$ under these gas-phase conditions was observed as shown in Figure 4.

As in the cases of the oligomerization reactions of $H_2C{=}CHCO_2CH_3$ initiated by F_3C^- and $C_3H_5^-$, the same rate constants for the decay of m/z 40 and 81 were obtained under both sets of conditions, indicating no P_{He} dependency on the initiation step. If both $NCCH_2^-$ and $NCCH_2^-(CH_3CN)$ serve as initiator anions, we would not expect both to exhibit the same decay rate constants. Cluster formation between an anion and its conjugate acid should reduce the rate constant of the clustered anion vs. that of the naked anion in nucleophilic reactions.[20] Therefore, it is most likely that reaction of $NCCH_2^-$ with $H_2C{=}CHCO_2CH_3$ successfully competes with clustering of $NCCH_2^-$ with CH_3CN (→ m/z 81) and leads to the same decay rate constant for both m/z 40 and 81. On the basis of this argument, we consider that $NCCH_2^-$ was the only initiator species in this oligomerization reaction.

The similar features of Figure 4 compared to Figures 2 and 3 are (a) the sequential production of the oligomeric anions m/z 126, 212, and 298 ($\delta m/z$ 86) and (b) loss of CH_3OH from the trimeric anion m/z 298 to yield m/z 266. Another similarity appears in Figures 3 and 4 in that (c) an anion (m/z 95 and 94, respectively) apparently derived from 1,2-addition followed by loss of CH_3OH in the initiation step was observed. Major differences found in data in Figure 4 compared to the previous two oligomerizations are (d) formation of two anions, m/z 180 and 352, by processes not observed before.

Formation of the minor steady-state amount (~1% of total product-ion signals) of anion m/z 94 was considered to arise by 1,2-addition of $NCCH_2^-$ to the carbonyl group of $H_2C{=}CHCO_2CH_3$, producing **18** via a collision complex (eq 16). Fragmentation of **18** via the collision complex **19** would be expected to be followed by fast H^+ transfer and separation of the components of the resulting collision complex to give **20** + CH_3OH. That



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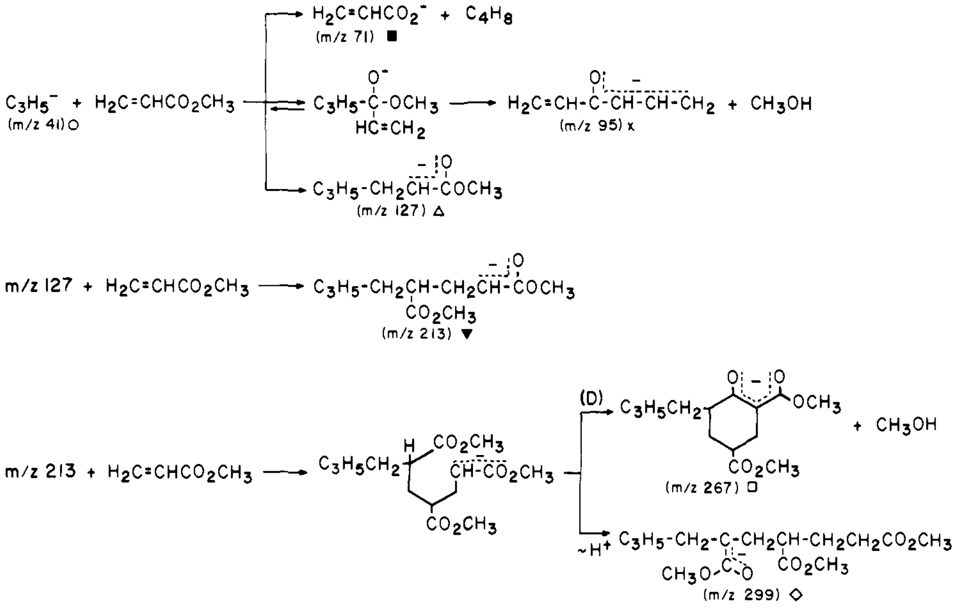
(18) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891.

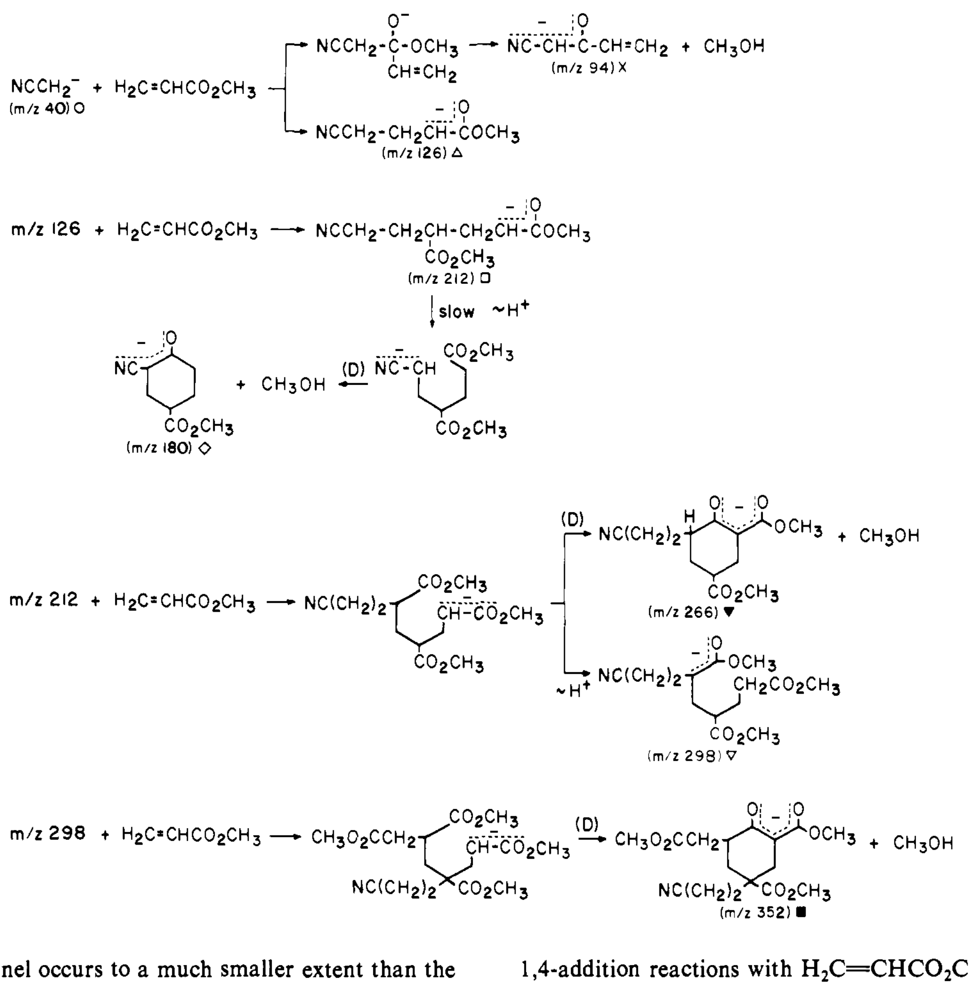
(19) Mackay et al. (Mackay, G. I.; Betowski, L. D.; Payzant, J. D.; Schiff, H. I.; Bohme, D. K. *J. Phys. Chem.* **1976**, *80*, 2919) give $k = 5.1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} for this H^+ transfer.

(20) Bohme, D. K.; Mackay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 978.

Scheme III



Scheme IV



this reaction channel occurs to a much smaller extent than the analogous channel (eq 11) observed in the oligomerization reaction initiated by $C_3H_5^-$ (see above) explains why a small steady-state concentration of the initiator $NCCH_2^-$ was not observed in the present system.

Generation of the anion *m/z* 180 could conceivably occur by addition of *m/z* 94 (**20**) to $H_2C{=}CHCO_2CH_3$ or by loss of CH_3OH from anion *m/z* 212. We consider that the stability of **20** through extensive delocalization would make either 1,2- or 1,4-addition reactions with $H_2C{=}CHCO_2CH_3$ endothermic.[21] While the structure of the dimeric anion *m/z* 212 (**21**) cannot

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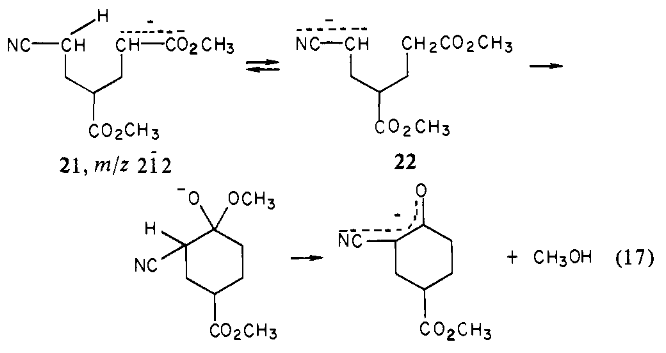
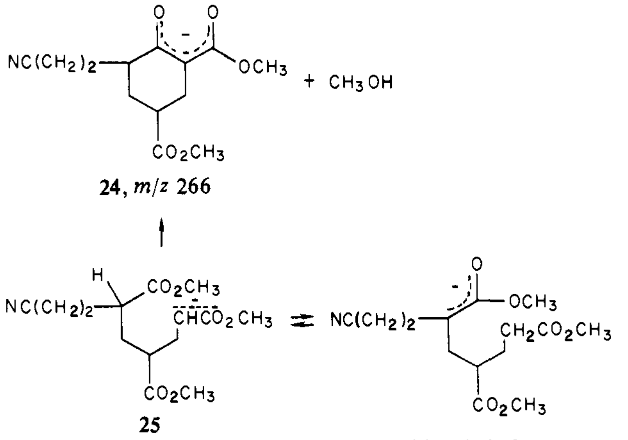
(21) ΔH_f° ($H_2C{=}CHC(O^-){=}CHCN$) = −34.0 kcal mol^{-1} (calcd)[10] assuming ΔH°_{acid} ($H_2C{=}CHC({=}O)CH_2CN$) = 336 kcal mol^{-1};[11] ΔH_f° ($H_2C{=}CHC({=}O)CH(CN)CH_2CH{=}C(O^-)OCH_3$) = −94.1 kcal mol^{-1} (calcd)[10] assuming ΔH°_{acid} ($H_2C{=}CHC({=}O)CH(CN)CH_2CH_2C({=}O)OCH_3$) = 371 kcal mol^{-1} as the simple ester enolate. From these values, we calculate ΔH° = +13.8 kcal mol^{-1} for the 1,4-addition reaction of $H_2C{=}CHC(O^-){=}CHCN$ to $H_2C{=}CHCO_2CH_3$; the 1,2-addition reaction should have a larger endothermicity.

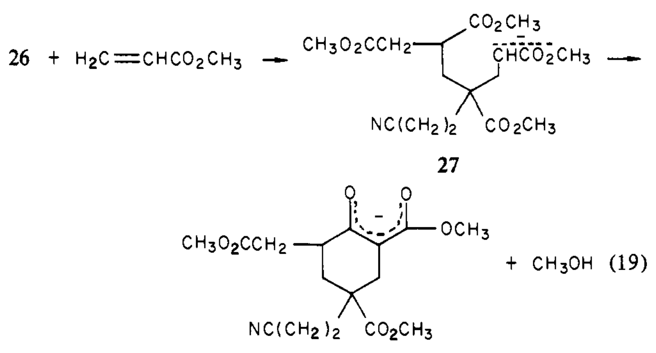

21, m/z 212
22
23, m/z 180
(17)

undergo a condensation reaction and expel CH_3OH, the intramolecular H^+ transfer of **21** → **22** could yield this necessary reaction sequence. This H^+ transfer would be slightly endothermic (1 to 2 kcal mol^{-1})[11] and produce the conjugate base of the cyclized β-keto nitrile **23** as the observed anion m/z 180. Although the intramolecular condensation of **22** to yield **23** and CH_3OH is expected to be very efficient (as in the Dieckmann cyclization of the conjugate base of dimethyl pimelate[13,14]), the intramolecular H^+ transfer from **21** → **22** must be quite inefficient[18] since only about 30% of the m/z 212 anions undergo this overall conversion during the early stages of the oligomerization process (Figure 4).

The telomerization of $H_2C{=}CHCO_2CH_3$ initiated by $NCCH_2^-$ was unique in that, for the first time, a tetrameric anionic species m/z 352 (tetramer − $CH_3OH)^-$ was observed in the latter stages of the process. Two possible sources of m/z 352 were considered: (i) addition of m/z 266 with $H_2C{=}CHCO_2CH_3$ or (ii) addition of m/z 298 to $H_2C{=}CHCO_2CH_3$ followed by intramolecular condensation and loss of CH_3OH. If we assume that the structure of m/z 266 is **24** by analogy with the (trimer − $CH_3OH)^-$ species deduced for the F_3C^-- and $C_3H_5^-$-initiated reactions, no further reaction of this highly delocalized anion with $H_2C{=}CHCO_2CH_3$ can occur due to the endothermicity of that reaction. However, the initially formed trimeric anion m/z 298 is considered to have structure **25** formed by a sequence of 1,4-addition reactions with $H_2C{=}CHCO_2CH_3$. Anion **25** can undergo the competitive intramolecular reactions of H^+ transfer to give the isomeric anion **26** (observed as m/z 298) and Dieckmann cyclization followed by loss of CH_3OH to yield **24**. As discussed earlier (see Table I and related discussion), the acidifying effect of the CN group is remote from the C–H bond of **25** involved in the intramolecular H^+ transfer. Thus, in this case, H^+ transfer between **25** and **26** is less favorable than between **4** and **6** (F_3C^- used as initiator) and a larger fraction of **25** is converted to **24** (m/z 266).


24, m/z 266
25
26, m/z 298
(18)

We believe that the reduced stability of the trimeric anion **26** compared to that of **6** allows for a slow 1,4-addition reaction of **26** with $H_2C{=}CHCO_2CH_3$ to give **27** (m/z 384), which undergoes Dieckmann cyclization and loss of CH_3OH to produce **28** (eq 19) as the observed (tetramer − $CH_3OH)^-$, m/z 352. The corresponding (tetramer − $CH_3OH)^-$ species was not observed from **6** even at larger concentrations of added $H_2C{=}CHCO_2CH_3$ (up to 10^{13} molecules cm^{-3}) than are shown in Figure 2 probably because of the greater stability of trimeric anion **6**. In the $C_3H_5^-$-initiated telomerization where formation of a related tetrameric species should also be observed on the basis of the above arguments, the amount of the trimeric anion **16** (m/z 299) is so small that formation of the corresponding tetrameric anion or (tetramer − $CH_3OH)^-$ would not be observed. Thus, the above arguments are self-consistent with the observations in these three related, although somewhat diverse, oligomerization reactions.


27
28, m/z 352
(19)

From the data and considerations given above, we arrive at the mechanism for the $NCCH_2^-$-initiated oligomerization of $H_2C{=}CHCO_2CH_3$ shown in Scheme IV with structural assignments for the various anionic species observed in Figure 4. A problem with computer simulation of the data in Figure 4 is that we "recover" only about 75% of ion products compared to the initiator (m/z 40 + m/z 81) signals. This is due to mass discrimination by the quadrupole mass spectrometer of the higher mass ions. In such cases, we seek to fit the simulated maxima of intermediate ion signals vs. concentration of neutral ($H_2C{=}CHCO_2CH_3$) added to that observed in Figure 4.[22] The generalized mechanism considered from Scheme IV is given in eq 20. The reasonably

$$\begin{gathered}\text{A } (m/z\ 40,\ 81) \xrightarrow{k_2} \text{B } (m/z\ 94)\\ \text{A } (m/z\ 40,\ 81) \xrightarrow{k_1} \text{C } (m/z\ 126) \xrightarrow{k_3} \text{D } (m/z\ 212)\\ \text{D } (m/z\ 212) \xrightarrow{k_4} \text{E } (m/z\ 180)\\ \text{D } (m/z\ 212) \xrightarrow{k_5} \text{F } (m/z)\ 266,\ 298,\ 352\end{gathered} \tag{20}$$

good fit of the data in Figure 4 was obtained by such computer simulation with the following rate constants: $k_1 = 4 \times 10^{-10}$, $k_2 = 1 \times 10^{-11}$, $k_3 = 5 \times 10^{-11}$, $k_4 = 1 \times 10^{-11}$, and $k_5 = 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Note that the rate constants for the propagation steps, k_3 and k_5, are the same (within expected error limits of ±50%) as those obtained for the F_3C^-- and $C_3H_5^-$-initiated oligomerizations of $H_2C{=}CHCO_2CH_3$ ($k_p = 4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}). This suggests that the nucleophilicity of the monomeric ($RCH_2CHCO_2CH_3^-$) and dimeric anions ($RCH_2CH(CO_2CH_3)CH_2CHCO_2CH_3^-$) toward conjugate 1,4-addition with $H_2C{=}CHCO_2CH_3$ show little or no kinetic influence by R as it is changed from the F_3C to the $NCCH_2$ and C_3H_5 groups.

Summary

The principal sequence of reactions observed in the gas-phase anionic oligomerizations of $H_2C{=}CHCO_2CH_3$ (MA) initiated by F_3C^-, $NCCH_2^-$, and $C_3H_5^-$ (In^-) involved 1,4-addition reactions to the vinyl monomer, $In^- + MA \rightarrow In\text{-}CH_2CHCO_2CH_3^- \xrightarrow{MA} In\text{-}CH_2CH(CO_2CH_3)CH_2CHCO_2CH_3^- \xrightarrow{MA} In(CH_2CH(CO_2CH_3))_2CH_2CHCO_2CH_3^-$. Termination of the oligomerization process occurred when the latter trimeric anion underwent com-

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[22] While mass discrimination can lead to errors in evaluating branching ratios for reactions, it is not important in determining the maxima of ion signals for intermediate species and rate constants in the consecutive pseudo-first-order processes described here; see ref 5a and 7b.

petitive, intramolecular H^+ transfer and Dieckmann cyclization with loss of CH_3OH. The relative amounts of these two termination reactions were strongly dependent on the structure of the initiator anion. Several other minor reactions were observed when $NCCH_2^-$ and $C_3H_5^-$ were used as initiators.

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Registry No. $H_2C{=}CHCO_2CH_3$, 96-33-3; F_3C^-, 54128-17-5; $C_3H_5^-$, 1724-46-5; $NCCH_2^-$, 21438-99-3.

Gas-Phase Acidity of Aliphatic Alcohols

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Abstract: The gas-phase acidities of aliphatic alcohols containing up to nine carbon atoms have been determined by the method of dissociation of proton-bound dimers. Alkyl substituent effects on acidity are discussed in terms of dipolar, polarizability, and hyperconjugation effects. The latter seems to account for the unexpected higher acidity observed for secondary alcohols with respect to the isomeric tertiary alcohols. The influence of through-space dipolar interactions is involved to account for the increasing acidity of the higher linear homologues.

Introduction

The dissociation of proton-bound dimer ions results in the formation of two products according to reaction 1. It has been

$$A_1HA_2^- \xrightarrow{k_1} A_1^- + A_2H \qquad (1a)$$

$$A_1HA_2^- \xrightarrow{k_2} A_2^- + A_1H \qquad (1b)$$

shown[1] that thermodynamic properties related to the acidities of A_1H and A_2H can be obtained from the relative intensities of A_1^- and A_2^- according to

$$\ln I(A_1^-)/I(A_2^-) = \ln k_1/k_2 = \Delta(\Delta G^\circ_{ac})/RT \qquad (2)$$

where $I(A_1^-)$ stands for the measured intensity of A_1^- and $\Delta(\Delta G^\circ_{ac})$ is the difference in gas-phase acidities between A_1H and A_2H, ΔG°_{ac} being defined as the change in free energy for the heterolytic cleavage reaction (3). Recently, there has been a

$$AH \rightarrow A^- + H^+ \qquad (3)$$

growing interest in the determination of molecular properties in isolated systems, and information on gas-phase basicities and acidities has become available, mostly from measurements of proton-transfer equilibria either in ion cyclotron resonance (ICR) or high-pressure mass spectrometric experiments (HPMS; see ref 2 for a recent review). The effects of alkyl groups on acidity have been considered in terms of inductive and polarization substituent effects.[3,4] It is now established that the stabilization of anions by alkyl substituents is due mostly to the role played by polarization forces between the charged center and the alkyl group. Destabilizing inductive effects operate at longer molecular distances and thus influence the stability of anions of a lesser extent. The possible role played by resonance effects such as hyperconjugation has also been considered in order to explain stabilization and isotope effects in anions.[5] However, some results[6] indicate that the effect of methyl groups on acidity seems to be difficult to predict also because there are relatively few data available on the acidic properties in the gas phase as compared to known basic properties.

In the course of recent studies of the reactions of alkoxide anions[7] we became interested in the acidities of aliphatic alcohols. We have applied the method of dissociation of proton-bound dimers to the determination of their relative acidities. The method of dissociation of proton-bound dimers was originally developed by Cooks and collaborators (see literature cited in ref 1), and it can represent a useful alternative to the ICR and HPMS methods. The method is based on the possibility for sampling decomposition products in a well-defined time domain of metastable decays given by the experimental parameters of a double-sector mass spectrometer operated in the MIKES mode.[8] It is assumed that the relative intensities of the products of metastable unimolecular decompositions can be directly related to their respective reaction rate constants of formation as represented in eq 2. Actually, this is based on the assumption that both rate constants k_1 and k_2 behave in an identical manner as a function of the internal energy in the system (see ref 1). Given the narrow time domain (hence corresponding to a narrow energy domain) sampled by the MIKES experiment and considering the similarities between the bonds being broken in the dissociation of proton-bound dimers, the above assumption can certainly be justified in these systems. However, competitive rearrangements and/or dissociation processes may alter the quantitation of the results: this has been reported in ref 1 for cases involving aliphatic ketones. The method of dissociation of proton-bound dimers can be the method of choice to study cases in which steady pressures required for equilibrium measurements

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