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^{13}C NMR Studies on Anion Pairs Related to Acrylate Polymerization. 2. Dimer Models

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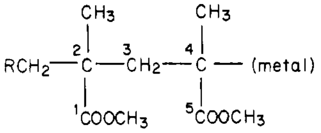
ABSTRACT: A ^{13}C NMR study has been made in tetrahydrofuran of model dimer anion pairs of methyl methacrylate formed by metalation of dimethyl 2,4-dimethylglutarate derivatives. The results at −20 °C resemble those found earlier for simpler monomeric models formed from isobutyric esters. Two isomers exist whose amounts depend on counterion as does the charge distribution between oxygen and carbon atoms. The lithium salt undergoes changes on cooling whose origins are not entirely clear. Attempts have been made to estimate diastereomer preference and to relate this to stereospecific polymerization of methyl methacrylate.

In part 1 of this series,[1] alkali metal derivatives of methyl isobutyrate, ethyl isobutyrate, and methyl 2-methylbutyrate were prepared as models of a simple one-unit growing chain in anionic methyl methacrylate polymerization. In tetrahydrofuran (THF) solution, examination by ^{13}C NMR spectroscopy showed that these compounds existed largely as enolate structures with some charge delocalized to carbon, to an increasing extent as counterion size becomes larger.

In the stereopolymerization of vinyl monomers the steric relation between the active and penultimate monomer units is an important parameter so it appeared of interest to study two-unit models with the terminal unit an active alkali metal derivative. The starting materials chosen were dimethyl 2-(methoxymethyl)-2,4-dimethylglutarate and dimethyl 2,2,4-trimethylglutarate. These could be metalated to form compounds



$$RCH_2-\underset{^{1}COOCH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{3}{C}H_2-\underset{^{5}COOCH_3}{\overset{CH_3}{\overset{4}{C}}}-(\mathrm{metal})$$

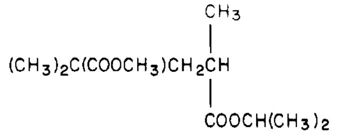
R = H or CH_3O

which are equivalent to two-unit growing chains in methyl methacrylate anionic polymerization.

Experimental Section

Dimethyl 2-(methoxymethyl)-2,4-dimethylglutarate (A) was prepared according to a published procedure[2] by refluxing a mixture of methanol and methyl methacrylate in the presence of sodium methoxide and hydroquinone. The methyl methacrylate dimer was separated from the mixture of products on a spinning-band column [bp 106 °C (6 mm)]. The dimer is an almost 1:1 mixture of meso and racemic forms as determined by capillary column gas chromatography. Similar results have been reported by Fujishige.[3]

Dimethyl 2,2,4-trimethylglutarate (B) was prepared from methyl lithioisobutyrate and an equimolar amount of methyl methacrylate. Methyl lithioisobutyrate from 6.54 g (64 mmol) of methyl isobutyrate was obtained as a white powder by metalation with an equivalent amount of i-Pr_2NLi in hexane. After removal of the volatile material by pumping, THF (100 mL) was distilled in from the vacuum line and methyl methacrylate (6.41 g, 64 mmol) was distilled in slowly (~4 h) (from a break seal attached to the flask) with vigorous stirring at −78 °C. When reaction was complete, methanol (2.2 g, 68.7 mmol) was distilled in, at which point the solution became viscous. The mixture was stirred and allowed to reach room temperature slowly and removed from the vacuum line. The volatiles were removed and the oily solid was extracted with diethyl ether and water. The ether layer was dried over Na_2SO_4 and subjected to vacuum distillation on a spinning-band column. A 45% yield of dimethyl 2,2,4 trimethylglutarate [bp 90 °C (6 mm)] was obtained. It is of interest to note that if 2-propanol is used as a protonating agent instead of methanol, considerable amounts of ester exchange appear to occur. The major product obtained was probably



$$(CH_3)_2C(COOCH_3)CH_2\underset{COOCH(CH_3)_2}{\overset{CH_3}{C}H}$$

as estimated by NMR analysis.

The dimers were metalated in the way described for butyric esters.[1] N-Lithiodiisopropylamide or N-lithioisopropylcyclohexylamide was used for lithiation, and silazane salts were used for preparation of sodium and potassium derivatives. Metalations were normally carried out in THF at −70 °C (dimer A). The solutions contain, therefore, an equivalent amount of regenerated amine. Metalation in hexane starting at −70 °C and allowing the temperature to reach −10 °C before pumping off volatiles allowed amine-free solutions to be obtained. This was the procedure followed for dimer B and two samples of dimer A. It was confirmed that residual amine had no effect on spectra.

^{13}C NMR spectra were determined in THF at low temperatures, some decomposition always occurring on warming above 0 °C. Attempts to make measurements on lithium salts in hexane or toluene failed due to insufficient solubility. NMR spectra were obtained with a Varian XL-100 spectrometer operating in the Fourier transform mode using proton broad-band decoupling with quadrature detection and an external ^{19}F lock. Spectra were referenced to the high-field resonance of THF, whose chemical shift was determined to be 26.2 ppm relative to Me_4Si. Off-resonance experiments were used to aid in the assignments. THF-d_8 was used as solvent in the cases where some signals are close to the normal THF positions.

Solvents were purified and dried according to procedures commonly used in anionic polymerization experiments[4] and stored on a vacuum line over CaH_2 (hexane) or Na–K alloy (THF).

Results and Discussion

The ^{13}C NMR shifts of the methyl methacrylate dimers A and B and their metalated products are given in Tables I and II. Apart from the greater complexity of the spectra which occasionally produced difficulty in making some assignments, as noted in the table, the general pattern resembles that observed with the simple metalated butyric esters. The signal from the nominally metalated carbon (C_4) appears in the range δ 60–72, considerably downfield of the parent ($\delta \sim 36$); the corresponding ester carbonyl signal appears at δ 162–165, upfield from the normal position at $\delta \sim 177$. The variation in C_4 shift with counterion closely parallels that observed[1] in metalated isobutyrate salts (with the exception noted below) and can be attributed to greater carbanion character with heavier alkali metals. The shifts of the "inactive" monomer unit show smaller changes.

In each case two forms of the compound exist as indicated by the doubling of most of the chemical shifts (Figure 1). At ~−20 °C, one isomer (β) has generally higher field

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Table I
^{13}C Chemical Shifts (ppm) for Dimer B and Its Derivatives in THF at ~ −20 °C[a]

X	C=O (1)	C=O (5)	C(4)	C(2)	CH_2-C(3)	CH_3-C(1)	CH_3-C(4)
H[b]	177.1	176.5	36.9	42.3	44.7	26.0 25.0	19.5
Li							
α	182.2	162.4	72.8	46.4	45.4	26.9	18.3
β	178.9	161.5	74.8?	43.8	44.9	25.7	17.8
Na							
α	180.6	165.7	68.6	46.0	46.8	26.9	18.5
β	179.0	163.5	67.2	43.8	45.2	25.7	17.6
K							
α	180.3	164.3	63.9	45.6	47.6	26.7	18.6
β	179.8	162.7	62.2	45.1	46.8	25.8	19.5

[a] Ester methyl signals occur between 50.8 and 55.8 ppm, which can in some cases be assigned to specific structures. [b] At 25 °C.

Table II
^{13}C Chemical Shifts (ppm) for Dimer A and Its Derivatives at ~ −20 °C[a]

X	C=O (1)	C=O (5)	C(4)	C(2)	CH_2- (3)	CH_3- (1)	CH_3- (4)
H[b]	176.7	175.3	36.4 36.2	46.7	40.1 40.0	20.7 20.0	19.9 19.5
Li							
α	179.3	162.3	72.4	50.3	40.6	21.1	17.6
β	176.9	161.2	?	49.1	40.6	19.9	18.2
Na							
α	178.8	165.2	66.9	50.9	41.9	21.1	18.3
β	177.2	163.0	64.7	49.6	41.1	19.9	18.3?
K							
α	178.2	163.9	61.8?	?	42.3?	20.7?	18.6
β	177.8	162.7	59.8	50.4	42.3	20.7	19.6

[a] Separate signals from meso and racemic isomers can be observed in the parent compound with some carbons. According to ref 3, the lower field shifts can be assigned to the meso isomer. [b] At 25 °C.

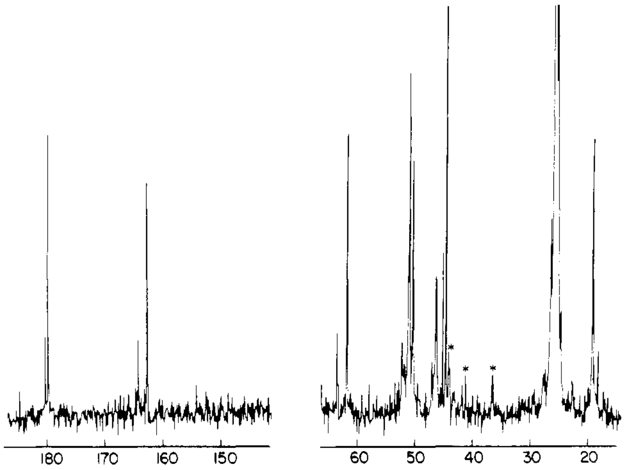


Figure 1. ^{13}C NMR spectrum of the potassium salt of dimer B in THF at −20 °C. Asterisks correspond to peaks of residual dimer.

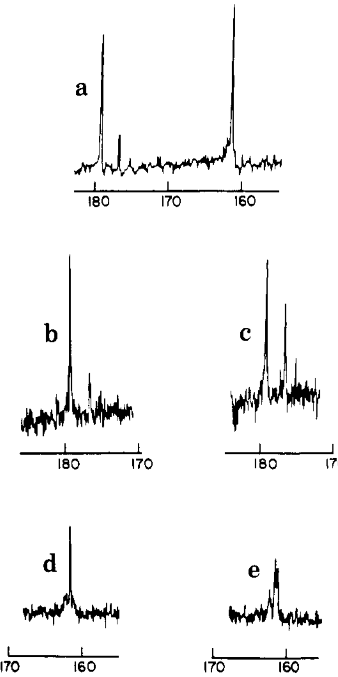


Figure 2. (a) Carbonyl region of the lithium salt of dimer A. Metalated in THF and never warmed (−60 °C). (b) Back carbonyl signal (C_1) of the lithium salt of dimer A prepared in THF and never warmed (−60 °C). (c) Same as (b) after warming to −20 °C and recooling to −60 °C. (d) Active carbonyl signal (C_5) of the lithium salt of dimer A prepared in THF and never warmed (−60 °C). Same as (d) after warming to −20 °C and recooling to −60 °C.

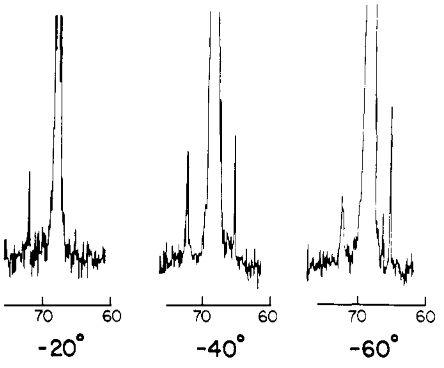
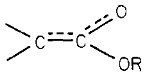


Figure 3. C_4 signal of the lithium salt of dimer A prepared in hexane and transferred to THF at low temperature. Changes as the solution is warmed. The broad signal is the low-field THF resonance. Gain ~1/3 at −20 °C compared to lower temperatures.

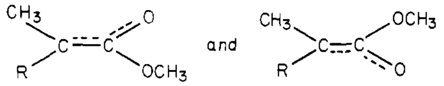
shifts and predominates (~80%) with potassium derivatives but the preference is reversed for lithium (~65% α) and sodium (55–60% α). Lowering the temperature increased the preference slightly for sodium and potassium compounds but the lithiated dimers showed more complex spectral changes which are more difficult to interpret. Specimens prepared by metalation in THF at low temperatures originally showed at these temperatures almost pure isomer α present (>80%) but with a C_4 chemical shift of 65.0 ppm rather than 72.4 ppm and the corresponding C(O) shift at 161.6 ppm rather than 162.3 ppm (cf. Table I). On warming, the shifts changed to the normal values, both sets being present at intermediate temperatures. On recooling, the signals at 65.0 and 161.6 ppm reappeared without complete disappearance of the 72.4- and 162.3-ppm signals. Signals due to the β isomer also were evident. Three signals were therefore then visible in the 160-ppm region: 162.3, 161.6 (α), and 161.2 (β) ppm (Figure 2). The metalation product as formed at low temperatures is obviously not in equilibrium; only on warming does the β isomer, for instance, appear in normal amounts.

Samples metalated in hexane which had been warmed to remove solvent and amine before being transferred to THF at low temperatures showed similar phenomena except that the more mixed structure was visible from the beginning (Figure 3).

The presence in these compounds of two different species could have two causes. First, in dimer A at least, diastereomers could be present. Evidence on the salts of simple butyric esters has indicated that the



system is planar with very restricted rotation about the C–C bond; i.e., the structures most closely resemble enolate ions. In this case the counterion's position can be on either side of the planar system. If positional exchange is slow on the NMR time scale, then two diastereomers would be observed. Dimer B, however, has no asymmetric center on the inactive monomer unit and hence cannot show diastereoisomerism. Two isomers still exist, however, so the general phenomenon cannot be explained in these terms. The alkali metal salts of 2-methylbutyric acid esters also show the presence of two isomers



$R = C_2H_5$

so it seems likely that the same phenomenon occurs with the dimers, too, and that this is responsible for the observation of two isomers. With butyric salts no marked preference was observed for either isomer but in the dimers ($R = R'C(CH_3)(COOCH_3)CH_2$) the isomer preference depends on counterion and can be quite marked. Variation of the isomer ratio with temperature was also observed with the dimer salts but not with 2-methylbutyrate derivatives. Presumably the enthalpy difference is too small in the latter case.

Whereas the behavior of the sodium and potassium dimers follows a simple pattern, the lithiated dimer, although conforming to the same pattern at higher temperatures, shows more complex behavior at low temperatures. Isomer α at least, under these conditions, shows the presence of two forms with the carbons of the active center at 161.6/65.0 ppm besides the more normal 162.3/72.4 pair. In the former the C_4 shift is at abnormally high field compared with that of the simple lithiated esters but is in a normal position in the latter.

The higher field C_4 signal could be produced by increased carbanion character associated with a six-membered-ring complex involving the counterion and the penultimate ester group. Structures involving ester group complexes have been suggested orginally in hydrocarbon solvents[5,6] and even in polar solvents.[7,8] There appears to be no change in the signal from the penultimate carbonyl group, however, which might be expected from this type of coordination. Nor in the lithium derivative of dimer B at low temperatures is there evidence for splitting of the signal from the gem-dimethyl groups as expected from the formation of an asymmetric active center of relatively long lifetime. Only unequal signals at 26.9 (α) and 25.7 (β) ppm are visible as in the sodium derivative although interference by the solvent resonance (even in THF-d_8) prevents an unequivocal statement that no other signals exist. Conclusive evidence for a chelated structure is therefore absent although some change in structure of the lithiated dimer does occur at low temperatures. Some changes were observed with the lithium salts of isobutyric acid[1] which showed at low temperatures evidence for freezing in of rotation of the OCH_3 (or OC_2H_5) group. Doubling of some of the signals, including that of the metalated carbon, occurred. The difference in chemical shift at the latter position was, as expected, low (0.6–1.4 ppm) compared with the 7.4-ppm difference in lithiated dimers. The signals coalesced at higher temperatures whereas in the present case one simply replaced the other. The behavior of the two systems is therefore quite different.

In a further attempt to obtain alternative evidence for a diastereomer preference, the methyl iodide addition method of Hogen-Esch and co-workers was used.[9,10] In lithiated dimers of 2-vinylpyridine, cation-side attack occurs to give configuration retention. The lithium salt of dimer A prepared in THF at −78 °C was chosen as it shows the simplest structure if the temperature is never increased. Methyl-d_3 iodide was added slowly to it with vigorous stirring at the same temperature. The ^{13}C NMR spectrum of the isolated product gave signals attributed to the CH_3 group at the point of methyl iodide attack at 24.4 and 28.6 ppm in unequal proportion (2:1). (These two signals are, of course, of equal intensity if normal methyl iodide is used.) Signals from the CD_3 group were too weak to observe, presumably due to deuterium coupling and lack of an Overhauser effect). The results are consistent with some preference for one diastereomer at low temperatures under conditions where geometric isomer α is predominant. Unfortunately, we are not able to determine if this is the meso or racemic form. Nor are we able to determine the diastereomer preference of the β isomer.

At 0.2 M monomer, the lifetime of an active center between monomer additions at ~ -75 °C in THF will be ~ 0.03 s with sodium as counterion and about 0.5 s with lithium as judged from the rate data of Müller[7,8] and Yaddehiga.[11] The rate of $\alpha \rightleftharpoons \beta$ isomerization will be much slower. The preferred geometrical isomer will, therefore, be determined in the monomer addition step, will not be able to relax, and need not be that observed in the metalation reaction. Diastereomer exchange will be much faster. It can be estimated from the fact that only a single sharp signal from the *gem*-dimethyl groups is observed in all dimer B salts. Lifetimes would be at most fractional milliseconds assuming the 30-Hz separation between individual signals in the protonated material is applicable to alkali metal derivatives. Ample time is available for equilibration which sould be an important factor in stereostructure determination.

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