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Carbon-13 Nuclear Magnetic Resonance Studies on Anion Pairs Related to Acrylate Polymerization. 1. Monomeric Models

L. Vancea and S. Bywater*

Chemistry Division, National Research Council of Canada, Ottawa, Ontario K1A 0R9, Canada.

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ABSTRACT: Alkali metal derivatives of several butyric esters have been prepared and studied by ^{13}C NMR spectroscopy in tetrahydrofuran. These compounds are suitable models for the growing chain end in anionic methyl methacrylate polymerization. The results obtained suggest a planar structure largely enolate in character although carbanion character probably increases somewhat with the heavier alkali metals. Evidence for restricted rotation about the C–OR bond was found in the lithio esters at low temperatures.

In previous studies from this laboratory evidence on the nature of the active centers in anionic polymerization has been obtained from NMR studies of model anion pairs of low molecular weight. Among the compounds studied were derivatives of styrene,[1-3] α-methylstyrene,[1-3] isoprene,[3-6] and butadiene.[3,6] Normally these were one-unit models prepared by the addition of butyllithium to the corresponding monomer although occasionally models of higher degree of polymerization were also studied. Estimations of charge distribution, rotational barriers, and geometrical isomer preference could be obtained as a function of solvent and counterion. Similar experiments to characterize the nature of the active centers in methyl methacrylate polymerization could be of value. With this monomer, models cannot be formed simply by addition of butyllithium, for considerable attack on the ester function occurs also.[7] Suitable model alkali metal compounds can, however, be made by metalation of esters having a reactive hydrogen α to the ester function. For this purpose metalating agents such as *N*-lithiodiisopropylamide,[8,9] *N*-lithioisopropylcyclohexylamide,[10] and *N*-lithiobis(trimethylsilyl)amide[11] are especially suitable. The corresponding sodio[12] and potassio derivatives of the latter compound are also easily prepared to enable counterion effects to be studied after metalation. The esters studied as models were methyl and ethyl isobutyrate and methyl 2-methylbutyrate. An infrared study of the alkali metal derivatives of ethyl isobutyrate has already been made.[13]

Experimental Section

The *N*-lithio amides were prepared by reacting a slight excess of the free amine with *n*-butyllithium in hexane.[14] *N*-Sodiobis(trimethylsilyl)amide was prepared by using $NaNH_2$ in refluxing benzene.[15] The potassium derivative was prepared by using KNH_2[16] (freed from oil by repeated washing with dried hexane) in tetrahydrofuran at room temperature. After reaction, solvents and residual amines were removed under vacuum. Methyl isobutyrate (Eastman), ethyl isobutyrate (Aldrich), and *tert*-butyl acetate were commercial samples and were used as received. Methyl 2-methylbutyrate was prepared from the corresponding acid and methanol with concentrated H_2SO_4 as catalyst. All were dried over Na_2SO_4 before use. Purity was checked by gas chromatography. *n*-Hexane and benzene were purified by treatment with sulfuric acid for several days, washed, and fractionated before storage over calcium hydride. Tetrahydrofuran (THF) was fractionally distilled from potassium and stored under vacuum on sodium–potassium alloy.

The alkali metal salts of the esters were prepared under vacuum, using break seal techniques to add reagents. The metalating agent and ester dissolved in hexane were mixed at −78 °C and stirred at this temperature for about 30 min. The temperature was allowed to rise slowly to between 0 and −20 °C, at which point the solvent and amine were pumped off, final drying being accomplished by pumping on the solid at room temperature. The resulting solids were then dissolved in tetrahydrofuran at −78 °C and filtered into NMR tubes.

Metalations of the esters with sodium or potassium silazanes proceeded smoothly under these conditions but the lithium derivative was not sufficiently reactive toward butyric esters although *tert*-butyl acetate could be successfully metalated. In this case therefore metalations were carried out with *N*-lithiodiisopropylamide or occasionally with *N*-lithioisopropylcyclohexylamide. Both were effective. In some cases free amine regenerated in the metalation reaction was incompletely removed. Duplicate experiments on amine-free solutions showed negligible effects of the amine on NMR spectra. Several of the metalated esters were reacted with H_2O at low temperatures. The NMR spectrum of the product was found to be that of the ester before metalation.

^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode, using proton broad-band decoupling with quadrature detection and an external ^{19}F lock. Spectral assignments were aided by an off-resonance technique. All shifts were referenced to the high-field THF resonance determined to occur at $\delta = 26.2$. The variation with temperature between −70 and −25 °C was 0.05 ppm and hence neglected. The temperature unit was calibrated with a thermocouple held coaxially in the NMR tube partially filled with methanol.

Results and Discussion

^{13}C NMR measurements on the alkali metal derivatives of the various esters were made in THF normally at −50 °C. In some cases measurements were also made at temperatures up to room temperature, where the compounds were sufficiently stable during the time required to run the spectra although evidence of some decomposition was often noticed. The results are tabulated in Table I. From the results it can be seen that replacement of a hydrogen atom α to the carbonyl group produces major changes in the spectrum. The metalated carbon resonance moves to much lower field than in the ester to an extent which depends on the alkali metal, e.g., ~38 ppm for Li, ~33 ppm for sodium, and ~29 ppm for potassium. The carbonyl resonance moves upfield to ~161 ppm from its normal position at ~176 ppm. Minor changes occur in the OCH_3 (or OCH_2CH_3) resonances (largest for Li at 5–6 ppm downfield). The alkyl groups attached to the α-carbon atom became nonequivalent, indicating that rotation about the >C–COOR bond is slow on the NMR time scale. Several of the lithium compounds were investigated at temperatures as high as room temperature but no evidence of rotation could be obtained.

In order to try to establish whether in fact rotation about this bond occurs on a longer time scale, we investigated the alkali metal derivatives of the methyl ester of 2-methylbutyric acid. In this case, separate cis and trans isomers will exist whose proportion could change with temperature if isomerization is possible:

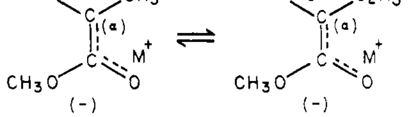

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Table I
Chemical Shifts of Parents and Metalated Esters in THF

		C(O)	C(α)	(OR)	CH_3	*T*, °C
methyl isobutyrate	(H)	176.6	34.4	51.3	19.2	30
	Li	160.0	73.1, 71.7	56.7, 55.8	17.6, 18.3	−60
	Li	160.5	72.3	56.4	17.6, 18.3	0
	Na	162.1	67.4	55.7	18.3, 18.5	−60
	K	161.2	62.9	53.0	18.4, 18.7	−50
ethyl isobutyrate	H	176.0	34.4	60.2, 14.5	19.2	30
	Li	159.5, 159.1	73.7, 73.1	65.7, 64.8, 15.8	17.6, 18.1	−50
	Li	159.6	73.0[b]	65.4, 65.0, 15.9	17.7, 18.3	10
	Na	161.1	68.7	64.3, 16.3	18.3, 18.4	−40
	K	160.7	65.6	62.0, 16.2	18.5, 18.5	−60
methyl 2-methylbutyrate	H	176.1	41.5	51.2	27.5;[a] 11.8, 16.9	30
	Li	160.0, 159.6	79.3, 79.9	56.8, 56.9	25.2;[a] 13.9, 14.2, 14.9, 15.1	−60
	Li	160.3, 159.9	78.9	56.8	25.1;[a] 13.8, 14.2, 14.9, 15.1	−20
	Na	162.1, 161.7	74.5, 74.6	55.8, 56.0	25.5, 25.6;[a] 13.9, 14.6, 15.1, 15.3	0
	K	161.3, 161.4	71.0, 70.4	54.0, 53.6	*a*, *c*; 14.4, 14.7, 15.3, 15.6	−60

[a] Methylene signals. [b] Broad. [c] Obscured.

The experiments in fact showed the presence of the two isomers in roughly equal amounts and whose proportion did not vary appreciably with temperature (±10%) between −60 and +20 °C. It appears therefore that either isomerization does not occur at a measurable rate or the enthalpy difference between the two isomers is quite small.

The observation of nonequivalent methyl groups in the isobutyrate salts parallels Rathke's observation[8] by ^1H NMR of nonequivalent hydrogens in *tert*-butyl lithioacetate in aromatic solvents and indicates considerable double-bond character in the >C–C(O) bond. We have confirmed these observations and also measured ^{13}C NMR spectra in both benzene and THF (benzene δ_{CH_2} 58.2, δ_C 76.7, δ_{CH_3} 28.8, $\delta_{C(O)}$ 164.4; THF, δ_{CH_2} 57.9, δ_C 74.5, δ_{CH_3} 29.0, $\delta_{C(O)}$ 165.5). Only with *tert*-butyl lithioacetate was solubility in aromatic hydrocarbons sufficient to measure spectra; corresponding isobutyrate salts were virtually insoluble.

Rathke's results were explained in terms of an oxygen–lithium-bonded enolate structure. It seems, however, likely that some delocalization of charge to carbon occurs in all these compounds. The C_α shifts are considerably upfield of the normal values for sp^2-hybridized carbons and to an increasing extent with the heavier alkali metals. This suggests that the carbanion character increases in the latter case. Similar results have been reported by House[17] for the anion pairs of phenyl acetone. With larger counterions, the cation diameter becomes commensurate in size with the heteroallylic system, which could induce a more even charge distribution. More exact determination of charge distribution as attempted in all-carbon systems[6] is difficult in the present systems due to difficulties in choosing a suitable uncharged reference compound.

The change in chemical shift of the α carbon from the parent ester is the result of two opposing trends, a downfield shift caused by the hybridization change $sp^3 \rightarrow sp^2$ (~100 ppm) and an upfield shift due to excess electron density delocalized to this position. The former effect predominates. In order to remove the first effect, suitable reference compounds having sp^2-hybridized carbons can often be found—enol acetates, for example, in the case of metalated ketones.[17] With these compounds the charge effect is estimated to be 19–25 ppm, which indicates a small fractional charge at the α carbon. A suitable reference for metalated butyric esters is not available but since the net downfield shift is smaller than for metalated ketones (particularly for the potassium compound) and the hybridization change is likely to be almost the same in the two cases, it can be concluded that charge at the α carbon may be somewhat greater for the metalated esters.

Previously reported[13] experiments on metalated ethyl isobutyrate showed a shift in the infrared band plausibly attributed to a C=C stretching mode from 1679 to 1652 cm^{-1} in moving from the lithium derivative to the potassium derivative in THF. These observations can be accommodated to the above interpretation of increasing enolate character with lithium if it is assumed that the increased frequency reflects an increase in π-bond order. A similar correlation explained in this manner was made for metalated 2,2-dimethyl-3-pentanone.[18]

With the lithium derivatives only of methyl and ethyl isobutyrate and at low temperatures, restricted rotation appears to occur about the C–OR bond. Methyl lithioisobutyrate, for example, shows two resonances for the $(O)CH_3$ and C(Li) carbons. The former coalesced at −31 °C, yielding a free energy of activation $\Delta G^{\ddagger}{}_{242}$ of 12.6 kcal mol^{-1}. At −1 °C the resonances appeared as single sharp lines. Similar behavior was observed for ethyl lithioisobutyrate. In this case the C(O) resonance also was doubled at low temperatures. Coalescence occurred at 0 °C, the C(Li) resonance at 10 °C, and the $(O)CH_2$ resonance almost coalesced at 10 °C.

The restricted rotation about the ester carbon–oxygen bond to relatively high temperature in the lithio esters is not normally observed in the parent esters. The presence of *s*-cis and *s*-trans forms of esters with the *s*-cis form (OR cis to the carbonyl group) predominating is a well-established phenomenon.[19] The barrier to rotation is normally too low to detect individual isomers by NMR methods except for *tert*-butyl formate, where in polar solvents below −94 °C separate ^1H signals for the formyl proton can be observed.[20] The presence of a bulky OR group appears to be necessary for observation of the isomers. In the present case, the barrier to rotation is obviously higher for the salts of ethyl isobutyrate than in those of methyl isobutyrate but is only observable in the lithium salts, at least down to −60 °C. The participation of resonance structures of the type $R—C(O^-)=O^+—R$ suggested[21] to explain the upfield carbonyl resonance in esters compared to ketones would produce restricted rotation about the C–OR bond. The present studies would therefore suggest that resonance structures of this type are more predominant in the lithium derivatives. It is noticeable that there the carbon resonance (OR) resonates 5 ppm downfield of that of the parent ester, which would be in agreement with this hypothesis. The difference is smaller with the sodium and potassium derivatives.

In summary, the present results suggest a planar structure

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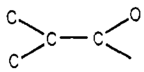

of predominant enolate character for the akali metal derivatives of butyric esters in THF, carbanion character increasing somewhat with the heavier alkali metals. The OR group must, however, have considerable freedom of rotation except for the lithium derivatives at low temperature, where complete planarity is attained of the whole structure.

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Carbon-13 Nuclear Magnetic Resonance Study of Ethylene–Butene Copolymers

G. Joseph Ray*

Research Department, Standard Oil Company (Indiana), Naperville, Illinois 60566

James Spanswick, Jack R. Knox, and Carl Serres

Research and Development Department, Amoco Chemicals Corporation, Naperville, Illinois 60566.

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ABSTRACT: The ^{13}C NMR spectra of ethylene–1-butene copolymers prepared by both a titanium and a vanadium catalyst system show peaks which can be assigned to a large number of sequences expected from copolymerization. We do not, however, detect any head-to-head polymerization of butene as reported recently. Moreover, we feel that peaks attributed to a head-to-head butene dyad are due rather to an isolated ethylene in a BEB sequence. Further, the three peaks observed in the methyl region of the spectrum are assigned to B-centered triads, as opposed to branches in positions having different tacticities as reported earlier. Finally, these data suggest that the ethyl brances in low-density polyethylene are not all isolated branches.

Introduction

Recently, Dechter and Mandelkern[1] (D–M) reported on the ^{13}C NMR spectrum of an ethylene–1-butene copolymer (hereafter referred to as ethylene–butene copolymer) containing about 10 mol % 1-butene. Their spectra clearly show the presence of 1,3-diethyl branching, as evidenced by several discrete peaks in their spectrum due to this moiety. They also claim to have 1,2-diethyl branches, which would arise from head-to-head polymerization of two butene units.

We have studied several ethylene–butene copolymers where the 1-butene level has ranged from 10 to 80 mol %. Furthermore, these polymers have been prepared with both a titanium-based catalyst system and a vanadium-based catalyst system. We have shown[2] that with ethylene–propylene copolymers the titanium catalyst gives isotactic propylene sequences and exclusively head-to-tail propylene polymerization even when up to two ethylene units are inserted between propylene units. On the other hand, vanadium catalyst causes an atactic polymerization of propylene and also gives tail-to-tail, as well as head-to-tail, propylene dyads. Head-to-head polymerization of propylene is usually not found in ethylene–propylene copolymers.[3]

We have analyzed our ethylene–butene copolymers in a manner analogous to that used for ethylene–propylene copolymers and, although we confirm the assignment of D–M for 1,3-diethyl branches, we see no evidence for 1,2-diethyl branches caused by head-to-head polymerization of butene. Instead, we feel that the peak at 24.57 ppm used by D–M for assignment of this branch type is due instead to the central methylene of a BEB sequence of a random ethylene–butene copolymer.

Experimental Section

Samples prepared with the titanium-based catalyst system were made by a small-scale copolymerization of ethylene and 1-butene carried out in 500-mL bottles at 70 °C and 25-psi comonomer pressure. The composition of the comonomers was held relatively constant by maintaining a 10 mol/h flow of gasses through the bottle.

Samples prepared with the vanadium-based catalyst were made by copolymerizing ethylene and 1-butene in a hexane solution at 1 atm and 25 °C. A soluble vanadium catalyst was used with ethylaluminum dichloride as a promoter. The composition of the copolymer was regulated by controlling the ratio of the monomers in the gas phase. Methanol was added to the hexane solution to precipitate the polymer after polymerization was completed.

Samples were prepared as approximately 30% (w/v) solutions in dideuteriotetrachloroethane and run at approximately 120 °C

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