Organometallic Chemistry

Alkali metal salts of acrylamide C_3H_4NOM (M = Li, Na, and K): synthesis and vibrational spectra

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Alkali metal salts of acrylamide C_3H_4NOM (M = Li, Na, and K) were synthesized for the first time by metallation of acrylamide with alkali metals, their alkyl derivatives, or hydrides. The structures of the compounds synthesized were studied by Raman and IR spectroscopy. Based on the results obtained, an ionic structure was proposed for the salts. The salts were tested as initiators of the anionic polymerization of acrylamide. The catalytic activity of C_3H_4NOM in the polymerization of acrylamide is not lower than that of the well known catalyst, $KOBu^t$.

Key words: acrylamide, alkali metals, salts; anionic polymerization; IR spectra, Raman spectra.

Numerous anionic-type catalysts are used in the polymerization of acrylamide, which occurs with the transfer of a proton (1,4-addition). These catalysts are metallic Na and Li, [1] *n*-butyllithium,[2] other organolithium compounds,[3] sodium *tert*-butoxide,[4–6] sodium amides,[5] organomagnesium compounds,[7,8] potassium ethoxide,[9] and sodium, magnesium, barium, and aluminum alkoxides.[10] In our opinion, all these catalysts act in an "indirect" manner, since proton exchange between them and acrylamide leads to the formation of the active sites in the reaction system that are responsible for the growth of the acrylamide chain.

$$\mathrm{ROM} + \mathrm{CH_2{=}CHCONH_2} \overset{K}{\rightleftharpoons}$$

$$\rightleftharpoons \mathrm{ROH} + \mathrm{CH_2{=}CHCONHM} \rightleftharpoons \mathrm{CH_2{=}CHCONH^-} + \mathrm{M^+}$$

M = Li, Na, K

The concentration of the active sites is determined by the position of the proton exchange equilibrium, whose equilibrium constant *K* depends on the basicities of the starting compounds and reaction products.

In the present work, we synthesized for the first time alkali metal salts of acrylamide, $CH_2{=}CHCONHLi$ (**1**), $CH_2{=}CHCONHNa$ (**2**), and $CH_2{=}CHCONHK$ (**3**), which could act as "direct" catalysts. Their structures were studied using vibrational spectroscopy. The salts obtained were tested as initiators of the anionic polymerization of acrylamide.

Results and Discussion

In order to synthesize salts **1**—**3**, we studied the metallation of acrylamide with alkali metals, their alkyl derivatives, and hydrides. In the case when alkali metals were used, the reaction proceeded smoothly and quanti-

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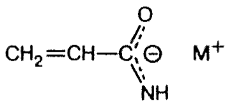
tatively in liquid ammonia at −40 to −33.5 °C and was completed over a period of 1—2 h. The reactions of acrylamide with lithium and sodium hydrides do not proceed to completion: no more than 60% of the NaH reacts with acrylamide, and less than 20% of the LiH is consumed. Apparently, this is due to the fact that the surface of the hydrides is covered with insoluble salts of acrylamide. At the same time, KH reacts with $CH_2{=}CHCONH_2$ in THF to give the corresponding K salt in a quantitative yield over a period of 0.5—1 h. A facile procedure for the preparation of the Li salt of acrylamide is metallation of acrylamide with *n*-butyllithium, which readily occurs at room temperature in benzene.

The alkali metal salts of acrylamide are insoluble in hydrocarbons and ethers; therefore, their purity depends substantially on the purity of the initial reactants.

All the salts synthesized by us were tested as catalysts for the anionic polymerization of acrylamide in an *N*-methylpyrrolidone solution at 100 °C (the concentration of the catalyst was 0.015 mol L^{-1} and that of acrylamide was 1.26 mol L^{-1}). Under these conditions, the catalytic activity of the alkali metal salts of acrylamide is not lower than that of the widely used potassium *tert*-butoxide, at comparable polymerization rates.

The vibrational spectra (IR and Raman) of the solid acrylamide and of salts **1—3** were obtained (Table 1). It can be seen from Table 1 that on going from acrylamide to its salts, the bands corresponding to the vibrations of the $CONH_2$ amide group disappear from the spectra, and a broad doublet band in the 1540—1570 cm^{-1} region and a narrow $\nu(NH)$ band at ~3300 cm^{-1} appear instead. The absorption in the 1540—1570 cm^{-1} region is typical of compounds containing NCO^- (see Ref. 12) or OCO^- (see Ref. 13) anionic groups and corresponds to the antisymmetrical $\nu_{as}(NCO^-)$ vibration. The spectra of alkali metal caprolactamates $\overline{CO(CH_2)_5N}M$ (M = Li, Na, and K) that we studied previously[12] exhibited a similar $\nu_{as}(NCO^-)$ band. The fact that the bands corresponding to the amide group disappear from the spectrum and the bands due to vibrations of the charged NCO^- group arise indicates that the salts studied are ionic compounds.


$CH_2{=}CH{-}C(O)(NH)^{\ominus}\ M^+$

This structure of the salts was confirmed by measurement of their dissociation constants (K_{dis}) in *N*-methylpyrrolidone at 100 °C. For example, $K_{dis} = 4.5 \cdot 10^{-3}$ and $9.6 \cdot 10^{-3}$ mol L^{-1} for salts **2** and **3**, respectively.

The vibrational spectra of salts **1—3** exhibit two further new bands (in the 1150—1170 cm^{-1} and 800—750 cm^{-1} ranges) that are not recorded in the spectra of acrylamide. The high intensity of the band at ~1160 cm^{-1} in the Raman spectra (Fig. 1) allows this band to be

Table 1. Vibrational spectra (ν/cm^{-1}) of $CH_2{=}CHCONHM$ (M = H, Li, Na, K)

M = H			M = K		M = Na		M = Li,	Assignment
IR	Raman	assignment*	IR	Raman	IR	Raman	IR	
3370 vs, br		$\nu(NH_2)$			3370 w, br		3370 br	$\nu(NH_2)$
			3294 m		3320 w			$\nu(NH)$
3200 vs, br		$\nu(NH_2)$			3200 br		3200 br	$\nu(NH_2)$
			3082 m					$\nu(CH)$
1688 s, br	1685 w	$\nu(CO)$			1665 sh		1670 sh	$\nu(CO)$
	1639 s	$\nu(C{=}C)$	1637 m	1637 s	1636 m	1631 s	1639 m	$\nu(C{=}C)$
1620 s	1600 w, br	$\delta(NH_2)$						
			1534 s, br	1530 w, br	1543 vs, br	1533 w	1567 s	$\nu(NCO^-)$
					1550 vs		1545 s	
1433 s	1438 s	$\delta(CH_2)$		1436 s		1436 s		$\delta(CH_2)$
1366 m		$\delta(CH)$						
1283 m	1289 s	$\nu(CN)$	1280 m	1290 w	1286 w	1277 w	1290 w	$\delta(CH)$
			1176 s	1170 s	1161 s	1156 s	1176 s	$\nu(NCO^-)$
							1164 s	
1138 s	1130 w	$\delta(NH_2)$						
1060 w	1057 w	$\delta(CH_2)$	1050 w		1061 w		1083 m	$\delta(CH_2)$
							1059 m	
							1011 m	
993 m		$\nu(C{-}C)$	996 m		986 m		981 w	$\nu(C{-}C)$
961 s		$\rho(CH_2)$	946 s		946 s		946 m	$\rho({=}CH_2)$
849 m		$\delta(NH_2)$	860 w		856 w		860 vw	$\rho(NH)$
822 m		$\rho({=}CH)$	835 w		832 w		830 vw	$\rho({=}CH)$
			801 m		804 m		790 m, br	$\delta(NCO^-)$
			796 m		795 m			

* The frequencies of acrylamide were assigned using published data.[11]

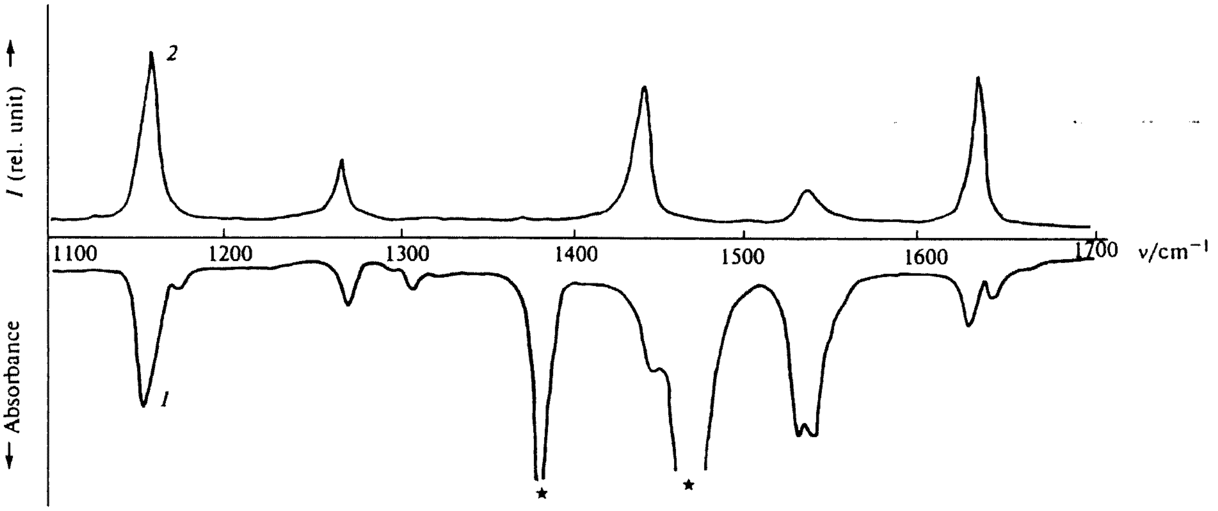


Fig. 1. IR (*1*) and Raman (*2*) spectra of the sodium salt of acrylamide (the asterisks mark the bands corresponding to the Vaseline oil).

assigned to the symmetrical vibration of the charged NCO^- group. The $\nu_s(NCO^-)$ band in the spectra of acrylamide salts is located at a markedly lower frequency than those in the spectra of alkali metal caprolactamates (1410—1390 cm^{-1}),[12] which may be due either to a change in the $N—C—O^-$ bond angle or to the fact that in the case of acrylamide salts, this vibration involves the proton at the N atom. The medium-intensity band in the 800—750 cm^{-1} region probably corresponds to the deformation vibration of the NCO^- group.

The assignment of the other bands in the spectra of the salts is presented in Table 1. It can be seen that the formation of the salt has only a slight effect on the spectral pattern corresponding to the $CH_2{=}CH—$ fragment. The frequency of vibrations of the double bond virtually does not change (~1639 cm^{-1}), and the frequency of the $\rho({=}CH_2)$ out-of-plane deformation vibration decreases by 15 cm^{-1}.

Judging from the spectra, the salt **3** prepared from potassium hydride is the purest sample. The spectra of other salts contain weak bands corresponding to the vibrations of the $CONH_2$ amide group at 1670 cm^{-1} (ν(CO)) and doublets at 3370 and 3200 cm^{-1} ($\nu(NH_2)$). When the sample is kept in air, the intensities of these bands increase, while those of the bands at ~1560 and ~1160 cm^{-1} decrease with time. The occurrence of bands corresponding to vibrations of acrylamide in the spectra of the salts is caused either by the presence of unreacted acrylamide in the reaction product or by partial hydrolysis of the salt.

Experimental

IR spectra were recorded in the 4000—600 cm^{-1} region (in Vaseline oil for salts **1**—**3** or in KBr pellets for the initial acrylamide) on a Bruker IFS-25 FTIR spectrometer with a resolution of 2 cm^{-1}. The Raman spectra were obtained in the 1800—1000 cm^{-1} region for solid samples in sealed glass ampules on a Ramanor-HG-2S spectrometer with an Ar^+ laser (λ = 5145 Å, W = 100 MW).

All the experiments, including the preparation of samples for IR and Raman spectroscopy, were carried out in an atmosphere of dry argon. The solvents were purified and dried by standard procedures.[14] Commercial samples of alkali metal hydrides (94% purity for LiH and 96% purity for NaH and KH) were used.

The lithium salt of acrylamide, C_3H_4NOLi. *A.* Dry crystalline acrylamide (5.0 g, 0.071 mol) dissolved in 100 mL of dried liquid ammonia was placed in a four-necked flask equipped with a stirrer, a reflux condenser cooled with solid CO_2, and a thermometer and maintained at −40 °C. Metallic Li (0.5 g, 0.07 mol) was added in several portions with stirring. The reaction of acrylamide with Li occurred much more slowly than the reactions with Na or K. The process was completed when the last pieces of Li disappeared (2 h). After evaporation of the ammonia, the solid residue was dried in the vacuum of a water-jet pump for 1 h at 50 °C and then kept for 1 h under a pressure of 1 Torr at 50 °C to give 5.3 g (0.069 mol) of C_3H_4NOLi as a white powder, yield 98.8%. Found (%): C, 46.23; H, 5.13; N, 18.90; Li, 8.92. C_3H_4LiNO. Calculated (%): C, 46.75; H, 5.19; N, 18.18; Li, 9.09.

B. Dry crystalline acrylamide (5.7 g, 0.08 mol) dissolved in 100 mL of anhydrous benzene was placed in a flask equipped with a stirrer, a reflux condenser, and a thermometer. At ~20 °C, a 1.5 *N* solution of Bu^nLi in benzene (53.5 mL, 0.08 mol) was added (the reaction mixture warmed up slightly). The mixture was boiled for 0.5 h and the precipitate was filtered off, washed with benzene (2×20), and dried successively in the vacuum of a water-jet pump and under a pressure of 1 Torr for 2 h at 50 °C to give 6.0 g (0.079 mol) of C_3H_4NOLi as a white powder, yield 97.4%. Found (%): C, 46.89; H, 5.21; N, 18.12; Li, 9.03. C_3H_4LiNO. Calculated (%): C, 46.75; H, 5.19; N, 18.18; Li, 9.09.

The potassium salt of acrylamide, C_3H_4NOK. *A.* Dry crystalline acrylamide (3.0 g, 0.042 mol) dissolved in 50 mL of dried liquid ammonia was placed in a four-necked flask equipped with a stirrer, a reflux condenser cooled with solid CO_2, and a thermometer and maintained at −40 °C. Metallic K (1.56 g, 0.04 mol) was added in several portions with stirring. The solution immediately changed to an intense blue color. As the alkali metal was consumed and the potassium salt was formed, the solution decolorized and a white solid precipitated in the reaction flask. The temperature of the reaction was maintained in the range from −40 to −33.5 °C (the boiling point of NH_3). After the addition of K was completed, the reaction mixture was stirred for an additional 0.5 h at −40 °C, and then the ammonia was evaporated and collected in a trap cooled with solid CO_2. (The collected dry ammonia can be used once again for the synthesis of alkali metal salts of acrylamide.) The solid residue was dried for 1 h in the vacuum of a water-jet pump at 50 °C and then for 1 h under a pressure of 1 Torr at 50 °C to give 4.3 g (0.039 mol) of C_3H_4NOK as a white powder, yield 99%. Found (%): C, 32.56; H, 3.63; N, 12.69; K, 35.48. C_3H_4KNO. Calculated (%): C, 32.99; H, 3.67; N, 12.83; K, 35.84.

B. KH (2.1 g, 0.052 mol) suspended in 50 mL of anhydrous THF was placed in a flask equipped with a stirrer, a reflux condenser, and a thermometer. The reaction mixture was cooled to −10 °C, and a solution of acrylamide (3.9 g, 0.055 mmol) in THF was added dropwise with stirring, while the gas evolution was monitored. The temperature of the reaction mixture was slowly raised to 0—5 °C, not interrupting the addition of the solution of acrylamide. As acrylamide was added, the suspension became thicker, and a plentiful white precipitate appeared in the flask. During the reaction, 0.05 mol of H_2 (1.13 L, 96% of the calculated amount of H_2) evolved. The suspension of the potassium salt was filtered and washed with THF; the solid residue was dried in the vacuum of a water-jet pump, and then for 2 h under a pressure of 1 Torr at 50 °C to give 5.4 g (0.049 mol) of C_3H_4NOK as a loose white powder, yield 97%. Found (%): C, 32.33; H, 3.61; N, 12.58; K, 35.53. C_3H_4KNO. Calculated (%): C, 32.99; H, 3.67; N, 12.83; K, 35.84.

The sodium salt of acrylamide, C_3H_4NONa. ***A.*** Dry crystalline acrylamide (6.0 g, 0.085 mol) dissolved in 100 mL of dried liquid ammonia was placed in a four-necked flask equipped with a stirrer, a reflux condenser cooled with solid CO_2, and a thermometer and maintained at −40 °C. Metallic Na (1.86 g, 0.081 mol) was added in several portions with stirring. The solution immediately changed to an intense blue color. As the alkali metal was consumed and the potassium salt was formed, the solution decolorized, and a plentiful loose white precipitate appeared in the reaction flask. The temperature of the reaction was maintained in the range from −40 to −33.5 °C. The further workup was similar to that described in the above procedures for the synthesis of the alkali metal salts of acrylamide according to method ***A***. This gave 7.8 g (0.084 mol) of C_3H_4NONa as a white powder, yield 98%. Found (%): C, 38.95; H, 4.22; N, 14.75; Na, 24.19. C_3H_4NNaO. Calculated (%): C, 38.71; H, 4.3; N, 15.05; Na, 24.73.

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