



Mechanochemical Synthesis of Urea Adducts with Long Chain Alkyl Derivatives

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Abstract. The adducts of urea and solid alkyl derivatives can be obtained mechanochemically in good yields. The products synthesized by grinding the solid reagents have identical IR spectra and XRD powder patterns to those obtained by crystallization from ethanolic solutions.

Key words: urea adducts; alkyl derivatives; mechanochemical synthesis

1. Introduction

When solutions of urea and straight-chain alkyl derivatives are mixed, colorless crystals of urea adducts are obtained [1]. These adducts correspond to hexagonal urea as a host for the alkyl chains which occupy parallel channels in the matrix [2]. The structure has been confirmed by XRD and neutron diffraction [2–5] and by NMR spectroscopy [6–7]. Infrared [8–10] and Raman [11–13] spectra are useful in detecting complex formation due to changes in the position and intensity of the urea bands.

The most general method of synthesis of urea clathrates is the use of a common solvent for the urea and alkyl derivative [1, 14]. A practical method is the addition of the alkyl derivative to a slurry of urea in a small amount of methanol, followed by stirring of the mixture [15]. Hollingsworth has reported that liquid suberonitrile can be clathrated by strong stirring with urea [16]. This method of synthesis can be expedited by the use of “activated” or “expanded” urea obtained by previous treatment with acetone [17–20].

In the pharmaceutical industry, certain alkyl derivatives, which are difficult to handle, are transformed into a suitable dry powder by grinding and tableting with urea [21]. One can infer that, here, a complex with urea has been formed mechanochemically. It is the purpose of this paper to present evidence, based on IR and

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XRD data that a mechanochemical synthesis of urea clathrates can be achieved in a simple and reliable way.

2. Experimental

The reagents were commercial products of analytical grade. The clathrates were made from ethanolic solutions [14–15] and mechanochemically. The weight ratio of urea to alkyl derivative was 3 : 1 in order to have an excess of the guest which favors a complete mechanochemical reaction. According to the ratio of the hexagonal urea channel length to the guest length the expected host/guest molar ratio is about 4.0 [22]. Samples of 1 g were ground by hand in an agate mortar (10 to 20 minutes), and in a stainless steel ball mill of the “wiggiebug” type (10 to 20 minutes). Larger samples of 5 g were milled in a Spex 8000D ball mill (0.5 to 1 hours) and in a high impact micronizer (Retzch) revolving at 20000 rpm leading to a 40 μm size powder grain. All samples prepared by the mechanochemical route were milled in the dry state and a moist state [14] (3% weight of water or methyl alcohol) and also with “activated urea” obtained from acetone solutions [20].

IR spectra were run in a FTIR spectrometer (ATI Mattson, Genesis Series) in Nujol mulls and in KBr disks. The Nujol mull technique was used in order to discard possible reactions of the sample with the KBr disks. The occurrence of mechanochemical reactions when analytes are milled and pressed with KBr to form disks suitable for IR spectroscopy is well known [23–25]. XRD patterns of the crystalline powders were recorded on a Siemens D5000 diffractometer using monochromatic $\text{CuK}\alpha$ radiation.

The following substances were used as guests: lauric acid, stearic acid, methyl stearate, cetyl alcohol, C_{28} and C_{30} mixture of alcohols, tetradecane, cetyl trimethyl ammonium bromide and polyethylene (of molecular weight 250 000). The chain lengths varied from 12 to 30 CH_2 units and the end groups were of different polarity and bulkiness: $-\text{CH}_3-\text{CH}_2\text{OH}$; $-\text{CO}_2\text{H}$; $-\text{CO}_2\text{CH}_3$ and $-\text{N}(\text{CH}_3)_3^+ \text{Br}^-$.

3. Results and Discussion

Evidence of clathrate formation was afforded by the IR and XRD patterns of the milled mixtures of urea with the alkyl derivatives in the dry state. Their IR and XRD patterns are the same as those of the products obtained from ethanolic solutions in our laboratory and also to those reported in the literature [2–5, 8–14, 20]. Figures 1 and 2 show the IR spectra and XRD powder patterns of the urea-stearic acid system, including the starting compounds and the complexes obtained from solutions and mechanochemically. IR spectra and XRD patterns of the complexes obtained from solutions and the milled mixture of the reagents are identical. In Table I XRD data are collected for this system. Similar evidence of clathrate formation is also obtained for the other studied systems, with the exception of polyethylene.

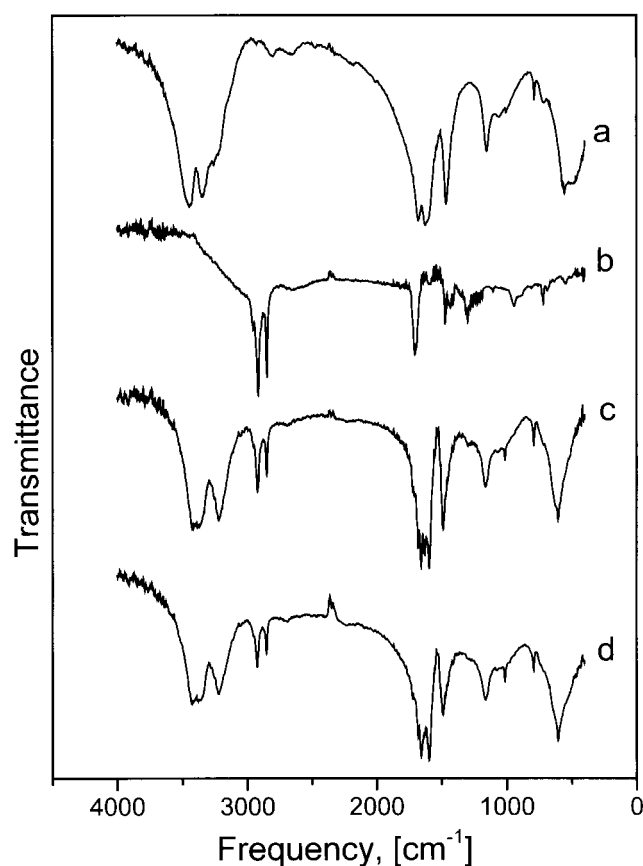


Figure 1. Infrared spectra in KBr of: (a) urea; (b) stearic acid; (c) urea-stearic acid clathrate obtained from ethanolic solution; (d) urea-stearic acid clathrate prepared by mechanical milling in the dry state.

The IR spectra of the complexes present strong absorption bands of urea in the hexagonal form and the CH_2 vibrations of the guest. These latter bands are not due to absorbed alkyl derivative since they are not removed by washing the solid with benzene. The XRD pattern is best suited for detecting unreacted urea, monitoring the strong reflection at $d = 3.97 \text{ \AA}$ ($2\theta = 22.38$). Over 90% conversion is achieved after 20 minutes of hand milling and in 10 minutes with the more efficient mechanical devices (vibrating ball mill, Spex 8000D and micronizer). The reaction proceeds to completion as can be observed in Figures 1 and 2. It is remarkable that the molecular ordering of host and guest molecules which takes place on crystallization from solutions can also be obtained by milling in the solid state. The entropic factor of the reaction in the solid state is unfavorable and the enthalpic contribution is weak, due to the difference in hydrogen bonding interaction between the hexagonal and tetragonal forms of urea and the differences in the hydrophobic interaction of the alkyl chains in the pure crystal and the complex. The

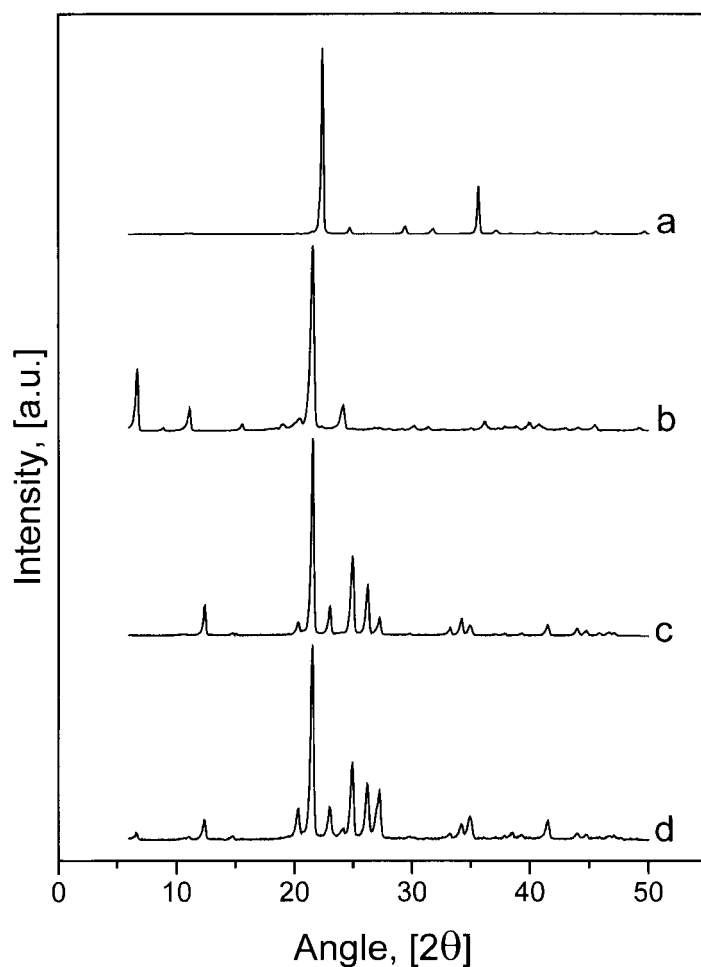


Figure 2. XRD powder patterns of: (a) urea; (b) stearic acid; (c) urea-stearic acid clathrate obtained from ethanolic solution; (d) urea-stearic acid clathrate prepared by mechanical milling in the dry state. The presence of weak diffraction peaks at 13.31 Å ($2\theta = 6.63$) and 3.69 Å ($2\theta = 24.10$) corresponds to an excess of stearic acid. These diffraction peaks disappear when the milled mixture is washed with benzene.

presence of small amounts of water and methyl alcohol (promoters) [1] accelerates the reaction which is completed after 5 minutes milling in the mortar. A similar effect occurs when “activated urea” obtained from acetone solution is employed [1].

The reaction with polyethylene was not possible at room temperature due to the soft nature of the polymer. Attempts to carry out this reaction were made by milling polyethylene cooled in liquid N_2 in the micronizer. No detectable formation of the complex was observed in the finely divided mixture (40 μm).

Table I. XRD powder data of urea, stearic acid and clathrates of urea-stearic acid prepared from ethanolic solution and by mechanical milling

Urea		Stearic Acid		Urea-Stearic Acid clathrate from ethanolic solution		Urea-Stearic Acid clathrate prepared by mechanical milling	
$d_{hkl}[\text{Å}]$	I [%]	$d_{hkl}[\text{Å}]$	I [%]	$d_{hkl}[\text{Å}]$	I [%]	$d_{hkl}[\text{Å}]$	I [%]
7.94	<1	13.25	33	8.40	<1	13.31*	5
4.67	<1	9.99	3	7.16	17	8.02	2
4.39	<1	7.98	9	6.00	2	7.15	7
4.13	2	5.69	4	5.58	<1	6.01	3
3.97	100	4.67	4	4.37	8	4.37	17
3.60	4	4.44	2	4.12	100	4.13	100
3.04	4	4.34	7	3.86	16	3.86	18
2.814	3	4.12	100	3.57	43	3.69*	4
2.621	<1	3.99	2	3.40	27	3.57	42
2.519	29	3.69	14	3.27	10	3.40	30
2.420	2	2.962	3	2.997	2	3.27	26
2.343	<1	2.850	3	2.918	<1	2.993	3
2.220	<1	2.742	<1	2.694	5	2.694	4
2.165	<1	2.617	<1	2.619	10	2.619	9
1.991	2	2.561	2	2.567	6	2.570	13
1.834	3	2.482	5	2.422	<1	2.420	<1
		2.406	<1	2.373	2	2.335	5
		2.375	<1	2.291	2	2.291	3
		2.255	5	2.174	6	2.174	6
		2.212	4	2.057	4	2.061	3
		2.104	2	2.023	3	2.022	3
		2.053	2	1.977	2	1.976	< 1
		1.993	4	1.945	2	1.946	2
		1.851	4	1.982	2	1.929	2

* Diffraction peaks corresponding to an excess of stearic acid. These peaks disappear when the milled mixture is washed with benzene.

4. Conclusions

Urea and different alkyl derivatives can form clathrates by grinding in the solid state. The mechanochemical reaction is accelerated by use of “activated” urea and by addition of a small amount of water or methyl alcohol. Polyethylene and urea do not react mechanochemically.

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