Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Studies of the Formation and Stability of Urea Inclusion Compounds

Jack Radell[a]
[a] Chemistry Research Laboratory Pitman-Dunn Research Laboratories Frankford Arsenal, Philadelphia, Pennsylvania

To cite this Article Radell, Jack(1968) 'Studies of the Formation and Stability of Urea Inclusion Compounds', Separation Science and Technology, 3: 3, 309 — 312
To link to this Article: DOI: 10.1080/01496396808052219
URL: http://dx.doi.org/10.1080/01496396808052219

SEPARATION SCIENCE, 3(3), pp. 309–312, June, 1968

NOTE

Studies of the Formation and Stability of Urea Inclusion Compounds

JACK RADELL
CHEMISTRY RESEARCH LABORATORY
PITMAN-DUNN RESEARCH LABORATORIES
FRANKFORD ARSENAL
PHILADELPHIA, PENNSYLVANIA

Summary

A study was undertaken to determine the relative ease of formation and stability of straight-chain primary and secondary alkanols capable of forming urea inclusion compounds. The compounds studied were 1-pentanol, 1-hexanol, 2-hexanol, 3-hexanol, 1-heptanol, 1-octanol, 3-octanol, 4-octanol, 1-nonanol, 4-nonanol, 5-nonanol, 1-decanol, 1-undecanol, and 1-dodecanol. 1-Heptanol was the shortest alcohol that formed an inclusion compound by the procedure employed. The ease of formation of a straight-chain alcohol was proportional to the number of uninterrupted methylene groups (—CH_2—) present. The ease of urea inclusion compound formation generally decreases as the functional group approaches the center of the chain. These conclusions were based on X-ray powder diffraction measurements and the weight of recovered products under equilibrium conditions.

DISCUSSION

A study was undertaken to determine the ease of formation and stability of straight-chain primary and secondary alkanols capable of forming urea inclusion compounds. The X-ray diffraction patterns and the weight of any solid material that formed on treatment of the alkanol with a urea methanol solution are listed in Table 1.

1-Pentanol, 1-hexanol, 2-hexanol, and 3-hexanol, when treated with urea, produced solid material which was shown to be free tetragonal urea from the X-ray data (Table 1) under the experimental

TABLE 1

X-Ray Powder Diffraction Patterns and Weight Data of Alkanol Urea Inclusion Compounds

Compound	2.61–2.63[a]	2.52–2.56	2.81–2.84	3.04–3.05	3.38–3.41	3.56–3.59	3.85–3.88	3.99–4.00	4.11–4.14	4.35–4.43	7.13–7.20	Weight isolated[b]
1-Pentanol	—	5	3	3	—	—	—	100	—	—	—	0.10
1-Hexanol	—	8	3	3	—	—	—	100	—	2	—	0.12
2-Hexanol	—	5	5	—	—	—	—	100	—	—	—	0.15
3-Hexanol	—	6	—	—	—	—	—	100	—	—	—	0.17
1-Heptanol	3[c]	3	—	—	3	10	1	100	12	3	6	0.10
1-Octanol	9	5	—	—	27	67	11	19	100	9	42	0.22
3-Octanol	7	7	4	12	17	81	9	69	100	—	63	0.20
4-Octanol	11	10	6	12	32	61	22	100	84	14	57	0.07
1-Nonanol	8	—	—	—	22	100	8	—	79	3	29	0.12
4-Nonanol	7	5	—	—	13	57	11	—	100	7	38	0.25
5-Nonanol	—	8	2	4	4	4	—	100	9	—	3	0.17
1-Decanol	8	4	—	—	19	83	12	—	100	6	34	0.20
1-Undecanol	6	—	—	—	10	100	5	—	52	—	24	0.25
1-Dodecanol	13	5	—	—	24	12	12	—	100	6	19	0.35
(Urea)	—	(7)	—	—	—	(6)	—	(100)	—	—	—	—

[a] Interplanar spacings in Angstroms, using CuK_α radiation.
[b] Grams of solid isolated per 1 g of guest.
[c] Relative intensities; 100 the strongest.

conditions described. The shortest *n*-alkanol forming a urea inclusion compound by the procedure employed was 1-heptanol. However, this compound was heavily contaminated by tetragonal urea, as indicated in Table 1 by the maximum intensity spacing at 3.99–4.00 Å characteristic of dissociated urea. The 1-heptanol urea inclusion compound gave characteristic spacings for a urea inclusion compound at 4.11, 3.57, and 7.13 Å. The 1-octanol, 3-octanol, and 4-octanol position isomers showed great difference in the ease with which their respective inclusion compounds were formed. The inclusion compound of 1-octanol formed more readily and the remaining isomers formed less readily.

Surprisingly, in the nonanol series the 4-nonanol formed the most inclusion compound, the 1-nonanol formed less, and the 5-nonanol formed the least. Based upon earlier reports (*1*), alcohols of varying complex-forming ability can be separated by using enough urea for complexing only the most readily formed component alcohol in the mixture. Obviously, this technique may be used to separate position isomers as well as members of a homologous series.

If we examine the various series of alcohols forming urea inclusion compounds, we find that those in which the hydroxyl group is placed in the center of the molecule or as close as possible to the center generally form the smallest quantity of urea inclusion compound. An increase in yield is usually obtained as the hydroxyl group is located closer to the end of the molecule. This is attributable to the fact that an increase in the cross-sectional diameter above that of a hydrocarbon in the planar zigzag conformation decreases the ease of urea inclusion compound-forming ability. When the alcohol on the straight chain is primary, no significant increase occurs in the planar zigzag conformation. In the same conformation the secondary alcohols of the straight-chain molecules have greater cross-sectional diameter. This does not distinguish the effect of the various secondary hydroxyls on the same carbon chain. From previous studies (2) it was found that the contribution to urea inclusion compound formation was enhanced not only by a greater number of methylene groups (*n*-octanol-1 versus *n*-nonanol-1) but by the greater number of uninterrupted methylene groups. The number of these uninterrupted methylene groups would permit us to distinguish the various secondary alcohols since the carbon to which the OH is attached is no longer a methylene carbon. Using this method, octanol has a maximum of eight uninterrupted methylene groups and 3-octanol has a maximum of five uninterrupted methylene groups. Also, the 3-octanol with a maximum of five uninterrupted methylene groups formed more inclusion compound than 4-octanol with a maximum of four uninterrupted methylene groups.

Consequently, the ease of separation of alkanol with an OH attached to a straight chain is directly related to the number of uninterrupted methylene groups. Obviously, a 1-alkanol will form more readily than a 2-alkanol. Similarly, by counting the number of uninterrupted methylene groups in two or more secondary alkanols, we can develop a procedure for separating such mixtures. The separation of tertiary alcohols from primary or secondary alcohols is simple, because tertiary alcohols do not form urea inclusion compounds at all.

EXPERIMENTAL

To 1 g of alkanol sample in a 4-dram screw-cap vial 4.5 ml of urea–methanol (0.15 g of urea per milliliter of methanol) solution was added. If the sample was a solid, the mixture was heated until it dissolved. If the sample was a liquid or a solid dissolved as described, the vial was capped and shaken vigorously for 5 sec and allowed to stand at room temperature for 4 hr and then at 5° for 18 hr. The sample was filtered with water aspirator suction onto a Hirsch funnel using a policeman to make a quantitative transfer. When all the sample was removed from the vial, the funnel was covered with a piece of rubber sheet (dental dam) making an air-tight seal which was pressed against the residue to express filtrate and to reduce the amount of mother liquor evaporating on the residue during the filtration. Using a rubber band to secure the rubber sheet around the funnel, the maximum aspirator suction was maintained for 5 min. The remaining solid was weighed and stored in a screw-cap vial.

A description of the X-ray equipment and techniques have been reported previously (3).

REFERENCES

1. E. Muller, *Methoden der Organischen Chemie* (*Houben-Weyl*), I/I George Thieme, Stuttgart, 1958, pp. 408–409.
2. J. Radell, J. W. Connolly, and L. D. Yuhas, *J. Org. Chem.*, **26**, 2022 (1961); J. Radell, J. W. Connolly, and W. R. Cosgrove, Jr., *J. Org. Chem.*, **26**, 2960 (1961).
3. J. Radell, B. W. Brodman, and E. D. Bergman, *Tetrahedron,* **20,** 13 (1964).

Received by editor April 1, 1968
Submitted for publication May 13, 1968