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

X-Ray Powder Diffraction Patterns of Some *n*-Alkanone Urea Inclusion Compounds

B. W. Brodman[a]; Jack Radell[a]
[a] Chemistry Research Laboratory, Pitman-Dunn Research Laboratories, Philadelphia, Pennsylvania

To cite this Article Brodman, B. W. and Radell, Jack(1967) 'X-Ray Powder Diffraction Patterns of Some *n*-Alkanone Urea Inclusion Compounds', Separation Science and Technology, 2: 1, 139 — 142
To link to this Article: DOI: 10.1080/01496396708049920
URL: http://dx.doi.org/10.1080/01496396708049920

SEPARATION SCIENCE, 2(1), 139–142 (1967)

NOTE

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B. W. BRODMAN and JACK RADELL
CHEMISTRY RESEARCH LABORATORY,
PITMAN-DUNN RESEARCH LABORATORIES,
FRANKFORD ARSENAL,
PHILADELPHIA, PENNSYLVANIA

Summary

The urea-inclusion-compound-forming ability of a series of closely related ketones was measured to determine the applicability of this procedure for separating and isolating the ketones. The results indicate this can be done.

To determine the feasibility of separating and isolating closely related *n*-alkanones, a study of the formation of crystalline urea inclusion compounds of straight-chain ketones was undertaken. Although other methods, such as vapor-phase chromatography, could be employed, the proposed method would be simpler for working with larger quantities of material. Earlier literature (*1*) has shown that normal ketones are capable of forming urea inclusion compounds starting with acetone. The use of urea inclusion compounds as a separation tool is particularly attractive because these compounds are easy to decompose to isolate the guest ketone trapped in the host molecule of urea. Such a process has potential commercial value, since the urea can be isolated and recycled. The nature of the urea inclusion compounds has been described in a recent review article (2).

DISCUSSION

The study of the X-ray powder patterns of the urea inclusion compounds of each of the ketones listed in Table 1 was undertaken to determine whether a crystalline complex had formed and whether the complex was contaminated with uncomplexed tetragonal urea.

This could be done from the X-ray data, as was shown earlier (*3*). In general, the stability of the urea inclusion compounds of a homologous family of straight-chain molecules increases, as does the chain length. This is true also of the ketones; 2-propanone* when treated with the urea-methanol solution formed no crystalline product. This fact is shown by the absence of interplanar spacings. 2-Butanone* treated similarly produced only pure uncomplexed urea. Urea is characterized by the spacings at 2.52 to 2.57, 2.81 to 2.83, 3.03 to 3.06; 3.63, and 3.96 to 4.03 Å (which is the most intense spacing). The peak at 2.52 to 2.57 Å is ambiguous because it is characteristic of both the tetragonal uncomplexed urea and the hexagonal urea inclusion compound.

The shortest chain ketone to form some inclusion compound was 2-pentanone. Although 2-pentanone was highly contaminated with uncomplexed urea, the peaks characteristic of the inclusion compound appeared weakly at 4.07 to 4.17 Å and 2.38 to 2.43 Å. The 3-pentanone showed no evidence for urea-inclusion-compound formation. This is consistant with an earlier postulate (*4*) stating

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* Although urea inclusion compounds have been previously reported by Truter (*1*), the procedure used in this work produced none.

TABLE 1

X-Ray Powder-Diffraction Patterns of Urea Inclusion Compounds of *n*-Alkanones

	1.93–1.95[a]	1.98–2.00	2.01–2.03	2.05–2.08	2.22–2.24	2.38–2.43	2.52–2.58	2.61–2.63	2.66–2.75	2.81–2.83
2-Propanone										
2-Butanone							0.13			0.04
2-Pentanone			0.04		0.04	0.07	0.15			0.07
3-Pentanone				0.32		0.12	0.11			
2-Hexanone		0.04	0.05	0.04	0.05	0.09	0.12	0.15	0.05	0.09
3-Hexanone	0.02[c]	0.04	0.05	0.05	0.04	0.07	0.13	0.13	0.15	0.08
2-Heptanone		0.02	0.02					0.02	0.08	
3-Heptanone			0.06				0.06	0.08	0.08	
4-Heptanone				0.07		0.07	0.07	0.14	0.12	
3-Octanone			0.06	0.04				0.11	0.11	
4-Octanone	0.04		0.04	0.05			0.05	0.09	0.09	
4-Nonanone	0.03	0.04	0.04	0.04				0.09	0.09	
5-Nonanone				0.03				0.03	0.05	
2-Decanone		0.03	0.04	0.07		0.02	0.03	0.11	0.05	
3-Decanone		0.05	0.05	0.07		0.03		0.08	0.07	
4-Decanone	0.03	0.04	0.04	0.04		0.04	0.04	0.10	0.11	
2-Umdecanone				0.08		0.08	0.07	0.16	0.11	

[a] Interplanar spacings in Å, using CuK_α radiation.

[b] Grams of solid isolated per 1 g of guest.

[c] Relative intensities; 1.00 the strongest.

that not only is there a requirement on the minimum number of methylene groups to form a urea inclusion compound but also that the uninterrupted sequence favors inclusion compound formation. The maximum uninterrupted sequence is four methylene groups for 2-pentanone and three for 3-pentanone. Both 2 and 3 hexanone are highly contaminated by uncomplexed urea but have much stronger interplanar spacing to characterize the urea inclusion compound than any smaller homologues previously mentioned. This trend continued, and the presence of some urea along with inclusion compound is verified by the X-ray data up to and including all the heptanones. The octanones are the shortest ketones converted to urea inclusion compounds in this study which were pure and uncontaminated by tetragonal urea.

Although this study did not include all theoretically possible position isomers, a large enough number of representative compounds have been examined to show a difference in the complex ability of the various ketones. This evidence is based upon the fact that the data in the table roughly relate the instability of the complex with the intensity of the uncomplexed urea (3) spacings. As a result, this work indicates that one could separate two ketones by such a technique. Closely related ketones might still be separated by using an amount of urea-methanol solution capable of combining

3.03–3.06	3.27–3.28	3.37–3.41	3.56–3.59	3.63	3.85–3.90	3.96–4.03	4.07–4.17	4.37	7.09–7.25	Grams of solid[b]
										0.00
0.04				0.04		1.00				0.08
0.15				0.11		1.00	0.03			0.10
0.33				0.13		1.00				0.25
0.15		0.17	1.00		0.17	1.00	0.02		0.78	0.18
0.15		0.21	0.84		0.55	1.00	0.53		0.21	0.28
0.03	0.02	0.21	0.92		0.11	0.11	1.00	0.03	0.45	0.23
0.10		0.06	1.00		0.08	0.29	0.79		0.64	0.28
0.12		0.50	0.81		0.12	0.45	1.00		0.51	0.26
		0.30	0.92		0.11		1.00	0.04	0.45	0.25
		0.16	1.00		0.05		0.74		0.46	0.35
	0.08	0.14	1.00		0.10	0.04	0.88		0.55	0.32
		0.11	1.00		0.06		0.52		0.30	0.34
	0.02	0.28	0.77		0.11		1,00	0.04	0.16	0.30
		0.18	0.50		0.05		1.00		0.30	0.33
	0.08	0.24	0.71		0.11		1.00	0.04	0.51	0.35
0.10		0.50	0.73		0.11		1.00		0.50	0.40

with the most stable ketone homologue only. This separation technique could be applied to isolate straight-chain ketones from branched ketones as well.

EXPERIMENTAL

The weight of complex isolated per gram of ketone used is reported in Table 1. The method used for preparing the urea inclusion complexes and the X-ray diffraction techniques have been previously described (5).

REFERENCES

1. E. V. Truter, *Wool Wax*, Cleaver-Hume, London, 1956, p. 212.
2. J. F. Brown, Jr., *Sci. Am.*, **207**, 82 (1962).
3. J. Radell and J. W. Connolly, in *Advances in X-Ray Analysis*, Vol. IV (W. M. Mueller, ed.), Plenum, New York, 1961, pp. 140–150.
4. J. Radell, J. W. Connolly, and W. R. Cosgrove, Jr., *J. Org. Chem.*, **26**, 2960 (1961).
5. J. Radell, B. W. Brodman, and E. D. Bergmann, *Tetrahedron*, **20**, 13 (1964).

Received by editor October 10, 1966
Submitted for publication October 20, 1966