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UREA INCLUSION COMPOUNDS OF n-ALKYL OXIRANES AND n-MERCAPTANS

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Abstract—The effect of a 1,2-epoxy group in a normal alkane on the urea inclusion compound forming ability of a molecule is negligible and consistent with the cross-sectional diameter of the molecule. 1,2-Epoxyoctane is the shortest homologue that formed an inclusion compound. X-ray powder diffraction patterns were used to verify the formation of the inclusion compounds and to determine their relative stability. Crystalline urea inclusion compounds of n-alkyl mercaptans were prepared. The formation of the complex was verified and relative stability determined from the X-ray powder diffraction data. The odour of the mercaptan guest in the urea host was never removed although diminished. None of the branched mercaptans tested formed a urea inclusion. n-Amyl mercaptan was the shortest homologue which formed a complex and n-decyl was the longest normal mercaptan tested.

INTRODUCTION

SINCE the maximum cross-sectional diameter of 1,2-epoxy-n-alkanes in the planar zigzag conformation is not significantly different from that of n-octane in the same conformation, the electronic effect of the oxirane function could be determined on the urea inclusion compound forming ability of the molecule. However, as in the case of the partially fluorinated esters[4] the effect of the oxirane group on the stability of the resulting complex appears to be related to the size of the molecule only.

In addition this research was undertaken to determine the shortest stable 1,2-epoxy-n-alkane urea inclusion compound which would be suitable for test as a mycological agent. It is anticipated that the slow decomposition of the urea host in a humid atmosphere will release the active oxirane compound at a desirable rate if the stability of the complex is controlled by including the appropriate homologue in the urea channel.

The study of urea inclusion compounds of n-alkyl mercaptans was undertaken for a variety of reasons all of which depended upon the removal of the mercaptan odour when trapped as a guest in a urea channel complex. This would reduce the odour hazard involved in storage and shipment once the urea complex was prepared. In addition the complexed mercaptans, if odourless, could be used as water detectors in organic systems because the water would decompose the urea host and release the mercaptan with its readily detectable odour. Unfortunately, even the slight vapour pressure of the mercaptan in the complex is sufficient to produce an easily detectable odour although less intense than the free mercaptan.

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[4] J. Radell and J. W. Connolly, *J. Org. Chem.* **25**, 1202 (1960).

DISCUSSION

Oxiranes. Although no difficulty was anticipated in the formation of an urea inclusion compound of an n-alkyl substituted oxirane, this investigation was undertaken to determine the shortest homologue which would form a complex and the relative stability of the members of the homologous series.

n-Octane, used as a standard, and 1,2-epoxyoctane were the shortest members of their respective families which formed a urea inclusion compound by the procedure used here. The urea inclusion compounds of these two molecules were heavily contaminated with tetragonal urea which formed by dissociation of the complex after the crystalline complex had separated from solution.[4,5]

From the relative concentration of the dissociated urea in both the epoxyoctane and octane compounds, the two complexes were found to have approximately the same stability. This similarity is attributable to the fact that the cross-sectional diameters are quite similar. Two additional and compensatory factors affecting the stability of the epoxyoctane complex in comparison with the octane complex are:

1. An increase in the stability of the 1,2-epoxyoctane complex due to the ionic interaction of the oxirane oxygen of the guest with the urea host.
2. A decrease in the stability of the epoxyoctane complex due to the decreased van der Waals stabilization because of the absence of two hydrogen atoms present in the parent alkane.

Dissociated or tetragonal urea was identified by the presence of a spacing at 3·95–4·01 Å which is the most intense spacing for urea. In addition interplanar spacings for urea occur, in decreasing order of importance at: 3·01–3·05, 2·13–2·18, 2·82–2·83 and 2·53–2·56 Å. The higher the relative intensity of the spacing for tetragonal urea, using 3·95–4·01 Å, the more dissociated urea is present and the less stable is the complex.[5,6] Therefore, the stability of a complex contaminated with dissociated urea is inversely proportional to the intensity of the spacing in the X-ray powder pattern for tetragonal urea when prepared as described.

The evidence for dissociated urea present along with the complexes of n-alkyl oxiranes rapidly diminishes and disappears as we proceed from 1,2-epoxyoctane to the higher homologues listed in the Table 1. Correspondingly, the crystalline material produced by all lower homologues proved to be dissociated tetragonal urea only. In general the relative intensity of the interplanar spacings of the dissociated urea is most reliable for determining relative stability of the complexes. This is due to the fact that the interplanar spacings characteristic of the complex change slightly for each homologue and their intensities are not useful for relative intensity measurements. The intensity of these spacings may even reverse for the more stable complexes of the higher homologues. This becomes evident if we examine the relative intensities in Table 1 for those interplanar spacings characteristic of the urea channel complex. These are in a descending order of importance: 4·11–4·15, 7·13–7·16, 3·39–3·40, 2·62–2·63, 2·06, 3·27–3·28, 2·69–2·70 and 4·34–4·37–4·37 A. The interplanar spacing at 3·56–3·57 Å is ambiguous being characteristic of both dissociated urea and complex. (The spacings for urea are included in Table 1) These spacings with minor variations have been found to be characteristic of all other urea inclusion compounds studied.

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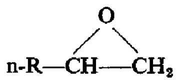
[5] J. Radell and J. W. Connolly, in W. M. Mueller, *Advances in X-Ray Analysis* Vol. IV, pp. 140–150. Plenum Press, New York (1961).

[6] J. Radell, J. W. Connolly and A. J. Raymond, *J. Amer. Chem. Soc.* **83**, 3958 (1961).

TABLE 1. X-RAY POWDER PATTERNS OF UREA INCLUSION COMPOUNDS OF n-R—CH—CH$_2$



$$\text{n-R—}\overset{\;\;\;\;\text{O}}{\text{CH—CH}_2}$$

n—R	2·06[a]	2·13–2·18	2·53–2·56	2·62–2·63	2·69–2·70	2·82–2.83	3·01–3·05	3·27–3·28	3·39 3·40	3·56–3·57	3·82–3·87	3·95–4·01	4·11–4·13	4·34–4·37	7·13–7·16
C_3H_7	—	—	0·06	—	—	—	0·11	—	—	—	—	1·00	—	—	—
C_5H_{11}	—	—	0·09	—	—	0·08	0·12	—	—	0·21	—	1·00	—	—	—
C_6H_{13}	0·17[b]	0·04	0·03	0·15	0·04	—	0·03	0·08	0·26	0·77	0·12	0·28	1·00	0·05	0·31
C_7H_{15}	0·04	0·03	—	0·04	0·04	—	—	0·04	0·12	1·00	0·06	0·06	0·45	0·03	0·31
$C_{10}H_{21}$	0·02	0·03	0·04	0·06	0·05	—	—	0·05	0·25	1·00	0·11	—	0·97	0·04	0·48
(Urea)	—	(0·08)	(0·05)	—	—	(0·06)	(0·24)	—	—	(0·10)	—	(1·00)	—	—	—

[a] Interplanar spacings in Å using CuK$_\alpha$ radiation.

[b] Relative intensities; 1·00 being the strongest.

The intensity of the 3·95–4·01 Å spacing characteristic of dissociated urea which first appears with the 1,2-epoxyoctane complex, rapidly diminishes and disappears as we proceed to the complexes of the higher homologues. 1,2-Epoxynonane shows only a slight (0·06) relative intensity for urea and 1,2-epoxydodecane shows none. Although the corresponding 1,2-epoxydecane and 1,2-epoxyundecane were not available, their complexes could safely be predicted to be free of urea since without exception, the complexes of the higher homologues of any series studied which formed complexes were more stable than all smaller homologues. Correspondingly, it can safely be predicted that the 1,2-epoxyhexane which was not available would not form any appreciable complex under the experimental conditions employed.

Mercaptans. The formation of the crystalline urea channel complexes of mercaptans was unequivocally confirmed by X-ray powder diffraction patterns. All the mercaptans studied were liquids. The relative intensity of these complexes could be estimated from the list of interplanar spacings found in Table 2. Several branched chain decyl mercaptans failed to form any urea channel complex and are not included in Table 2. The n-mercaptans studied were: butyl, amyl, hexyl, octyl and decyl. The X-ray data of the urea inclusion complexes of these compounds are listed in the Table 2 together with dissociated tetragonal urea for comparison.

TABLE 2. X-RAY POWDER PATTERNS OF UREA INCLUSION COMPOUNDS OF n = RSH

n-R	1·99[a]–2·02	2·51–2·54	2·60–2·63	3·03–3·06	3·36–3·41	3·54–3·56	3·97–4·01	4·07–4·11	7·01–7·18
C_4H_9	0·17[b]	0·48	—	0·17	0·05	—	1·00	—	—
C_5H_{11}	—	0·05	0·05	0·12	0·35	0·79	0·54	1·00	0·17
C_6H_{13}	0·08	0·06	0·09	0·05	0·28	0·53	0·21	1·00	0·26
C_8H_{17}	—	0·10	0·05	0·05	1·00	—	0·20	0·60	0·35
$C_{10}H_{21}$	0·06	—	—	—	0·09	—	0·40	0·40	0·42
(Urea)	(0·09)	(0·05)	—	(0·13)	—	(0·10)	(1·00)	—	—

[a] Interplanar spacing in Å using CuK_α radiation.
[b] Relative intensities; 1·00 being the strongest.

The most intense spacing usually used[4,6] which unequivocally characterizes dissociated tetragonal urea occurs at 3·97–4·01 Å. However, the spacing at 3·03–3·06 Å which is the next less intense spacing, also unequivocally characteristic of urea, is more useful for determining the relative intensity of the mercaptan. The latter spacing does not show the erratic behaviour of the 3·97–4·01 Å spacing evident from Table 2. At 3·97–4·01 Å the relative intensity for n-decyl mercaptan is 0·40 and not consistent with the previous values. At 3·03–3·06 Å the intensity for the same compound quite reasonably falls to zero. Except for this disagreement the relative intensity for the two spacings are in reasonably good agreement. The use of the interplanar spacing for dissociated urea is based upon the observation[5] that complexes filtered from a mother liquor are pure and dissociate only after filtration. The greater the intensity of the spacings characteristic of dissociated urea (tetragonal) the higher is the concentration of tetragonal urea and the less stable was the parent complex (hexagonal).

Butyl mercaptan which showed no evidence for complex formation had the most intense spacings for both 3·97–4·01 and 3·03–3·06 Å. Butyl mercaptan showed none of the complex spacings found in all other mercaptans listed which did form an isolatable complex.

The spacings characteristic of the hexagonal urea channel complex in decreasing order of intensity are: 4·07–4·11, 3·36–3·41, 7·01–7·18 and 2·60–2·63 Å. The 4·07–4·11 Å spacing although most intense it is not useful for determining relative intensity and exhibits very unusual behaviour. In previous studies[2] the intensity of the spacing at 4·07–4·11 Å for several homologous series increases with increasing chain length. In the mercaptans this previously observed behaviour is inverted and the intensity of the 4·07–4·11 Å spacing consistently decreases with increasing chain length. The most reliable urea complex spacing which appears for the mercaptan is at 7·01–7·18 Å. Here the intensity of the spacing is generally proportional to the chain length of the molecule. This spacing has the additional advantage of being unambiguously characteristic of the hexagonal channel complex.

Although none of the complexes of the mercaptans, even after thorough washing with ether was free of the mercaptan odour, it is possible the complexes of some of the higher homologues greater than n-decyl mercaptan may achieve this objective.

EXPERIMENTAL

Oxiranes and mercaptans. These compounds were all obtained from commercial sources.

Urea inclusion compounds. The inclusion compounds were prepared by a previously described procedure for measuring X-ray powder diffraction patterns.[4] To test whether the complexes of mercaptans were free of odour, the complexes obtained from the above procedure were washed with ether to remove any traces of the liquid mercaptan which may have adhered to the surface of the complex.

X-ray powder diffraction patterns. The interplanar spacing measurements were made as previously described.[4]