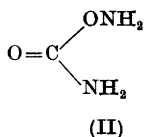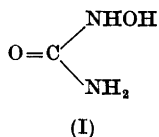# On the Isomerism of Hydroxyurea

IX. Absorption Spectra in the Infra-Red

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Absorption spectra in the frequency-region $3\,600-600$ cm^{-1} have been recorded of the two isomeric "oxyureas" melting at approximately 72°C (OU_{72}) and at approximately 140°C (OU_{140}), respectively [1].

The absorption spectrum of OU_{140} confirmed brief information previously published by other investigators [2]. It showed an intense, incompletely resolved pair of bands at about 1 650 cm^{-1}, similar to that produced by urea. It should undoubtedly, as also suggested by Runti and Deghenghi [2], be assigned to the carbonyl group.

$$O=C\begin{smallmatrix}NHOH\\\\NH_2\end{smallmatrix} \qquad O=C\begin{smallmatrix}ONH_2\\\\NH_2\end{smallmatrix}$$

(I)   (II)

Urea as well as the two "oxyureas" showed an identical set of bands at 3 300 $-3\,400$ cm^{-1}. These are tentatively assigned to N—H stretching vibrations. In the spectrum of OU_{140} there was observed an additional intense band at approximately 2 800 cm^{-1}, absent in the other two compounds. A possible assignment of this band to the (hydrogen-bonded) N—OH group would, together with the established carbonyl frequency, be in favour of formula (I) for OU_{140}. This structure can also account for most other physical and chemical properties (*vide, e. g.* previous publications in the present series) and may now be regarded as reasonably well established.

The IR-spectrum of OU_{72} has not previously been on record. In the region 1 500 -600 cm^{-1} it is much more complex than those of urea and OU_{140}. At higher frequencies it is similar to that of urea; it has, like urea, an intense absorption band in the carbonyl region (1 700 cm^{-1}). The strong absorption at 2 800 cm^{-1}, which was observed in OU_{140} is absent in OU_{72}. If the

assignment of this frequency to the N—OH group is correct it follows that OU_{72} does not contain a hydroxy-group. Since, furthermore, there seems to be evidence for a carbonyl group, the absorption spectrum appears to support the formula (II) for OU_{72}; this was recently proposed on the basis of classical chemical arguments by Exner [3].

The structure (II) is one of more than twenty formally possible combinations of hydroxylamine and cyanic acid, considered by the present author [5]. It can account for a number of the observed properties, such as the solubility in ether, which is greater than that of the isomeride (I), the existence of only one methoxyurea [6, p. 491] corresponding to structure (I), the absence of a colour reaction with ferric chloride, and finally also for the basic properties [7] of OU_{72} (weak, though stronger than those of urea) contrary to the weak acidic properties of OU_{140}. Other observations are, however, difficult to explain on the basis of structure (II), *e. g.* the polarographic properties [8] and the relative amounts of the isomerides formed in different solvents [9] by the reaction of hydroxylamine with cyanic acid. In these experiments it was found possible to correlate the isomerism with well-established knowledge on the tautomerism of cyanic acid. Structure I/II on the other hand implies that the structural ambiguity of cyanic acid is unimportant, and that the isomerism arises from the hydroxylamine molecule being added in two different manners to cyanic acid. These are, however, formalistic arguments, which may be weakened by future knowledge of the true reaction mechanism of the formation (*cf.* Ref.[10]).

Although plausible the formula (II) cannot be regarded as definitely proved. The classical chemical arguments [3,4] have the usual weaknesses characteristic for structure determination on the basis of chemical reactivity, and the absorption spectra need expert interpretation. Since the pressed-plate technique was employed, the spectral data refer to the crystalline state only.

A more detailed account of the spectroscopic investigations and the results of a kinetic examination of the rearrangement $OU_{72} \rightarrow OU_{140}$ will be presented in forthcoming publications.

1. Kofod, H. *Acta Chem. Scand.* **7** (1953) 938.
2. Runti, C. and Deghenghi, R. *Ann. Triestini* **22—23** (1952—53) sez. 2a, p. 9.
3. Exner, O. *Collection Czechoslov. Chem. Communs.* **22** (1957) 335.
4. Exner, O. *Chem. listy* **51** (1957) 497.
5. Kofod, H. *Final discussion. (In print).*
6. Kofod, H. *Acta Chem. Scand.* **8** (1954) 485, p. 486.
7. Kofod, H. *Acta Chem. Scand.* **8** (1954) 494.
8. Kofod, H. *Acta Chem. Scand.* **9** (1955) 455.
9. Kofod, H. *Acta Chem. Scand.* **10** (1956) 256.
10. Kofod, H. *Acta Chem. Scand.* **11** (1957) 5, p. 9.

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Table 1. Distribution of ^{90}Y between $CHCl_3$—DBP and 0.1 M HNO_3.

Conç. of DBP in $CHCl_3$ M	I_{aq} cpm	I_{org} cpm	log q	log K
0.003	1 471	13.1	—2.05	3.42
0.007	1 463	96.6	—1.18	3.19
0.01	1 162	276	—0.63	3.27
0.015	741	634	—0.07	3.31
0.02	457	900	+0.29	3.29
0.03	209	1 194	+0.76	3.23
0.05	47.3	1 493	+1.50	3.31
0.1	48.3	7 154	+2.17	3.07

Mean value: 3.26 ± 0.12

Separation of Strontium-90 and Yttrium-90 and the Preparation of Carrier-free Yttrium-90

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In investigations with the radioactive isotope ^{90}Sr it is often valuable to have a simple and rapid method of separating ^{90}Sr and its daughter ^{90}Y. Methods that have been used for this separation include ion exchange [1-3], precipitation [4-6], electrolysis [7], and solvent extraction [8-10]. As solvent extraction procedures usually are very efficient and rapid, it seemed worth while to develop such a method. Previously the TTA-benzene [8,9] and the DBP-dibutyl ether [10] systems have been used. As DBP (dibutyl phosphoric acid) extracts metal ions at lower pH values than TTA (thenoyl trifluoroacetone), we preferred to work out a procedure using DBP as a complexing agent.

The extraction with DBP and chloroform can also be used for the preparation of carrier-free ^{90}Y which is a suitable isotope for tracer experiments. A 0.1 M nitric acid solution of the long-lived parent ^{90}Sr will constitute a continuous supply of ^{90}Y.

Reagents. The fission product ^{90}Sr was obtained in 1 M HNO_3 from AERE, Harwell, England. ^{89}Sr was also purchased from Harwell as neutron-irradiated $SrCO_3$. The chloroform (analytical grade) was washed with water to remove the alcohol present. The di-*n*-butyl

phosphate (DBP) was kindly supplied by Albright & Wilson Ltd, London. Titration with alkali and analysis of C and H. (Found: C 45.0; H 8.7. Calc. for $C_8H_{19}PO_4$: C 45.7; H 9.1) showed the compound to be at least 99 % pure.

General procedure. The experiments were carried out at 25°C. The aqueous phase (5 ml) with 0.1 to 10 M HNO_3 and ^{90}Sr was shaken 3 to 5 minutes with an equal volume of 0.003 to 1 M DBP in chloroform. After centrifugation 0.1—0.5 ml of each phase was withdrawn. The dried samples were then counted with a total absorber thickness of 200 mg/cm². Corrections were made for counting efficiency, background, and the *bremsstrahlung* from ^{90}Sr.

Table 2. Distribution of ^{90}Y between 0.1 M DBP in $CHCl_3$ and HNO_3.

Conc. of HNO_3 in the aqueous phase M	I_{aq} cpm	I_{org} cpm	log q	log K
0.1	48.3	7 154	+2.17	3.07
0.15	119	7 890	+1.82	3.25
0.2	180	7 634	+1.63	3.44
0.3	762	6 818	+0.95	3.28
0.5	2 310	5 120	+0.35	3.35
0.7	4 667	2 505	—0.27	3.17
1	6 544	1 134	—0.76	3.14
1.5	7 183	298	—1.38	3.05
2	6 952	180	—1.59	3.22
3	7 144	110	—1.81	(3.52)
5	7 292	53.4	—2.14	(3.86)
5	7 857	72.2	—2.04	(3.96)
7	7 630	20.4	—2.57	(3.87)
7	7 776	18.5	—2.62	(3.82)
10	7 132	89.2	—1.90	(5.00)

Mean value: 3.22 ± 0.13