The nature of recoil selenium

The results undoubtedly show that the recoiled selenium which has not recombined is in an elementary state. Indeed, only elementary selenium is soluble in carbon disulphide and can be extracted by this agent. As, within the experimental error, the retention measured after liquid–liquid extraction is closely similar to the retention measured after an adsorption process, it is unlikely that selenium trioxide has been formed.

In many systems reduction on recoil is extensive, as is the case for permanganates, chromates and bromates. In this case part of the selenium recoil atoms are thus even reduced to an oxidation number zero. One must then admit, either that no stripping of oxygen ions, but only of oxygen atoms takes place during recoil, or, that while cooling down the recoil atom is the centre of a rearrangement of the crystal with a redistribution of electrons. The latter explanation seems less satisfactory, as a thorough rearrangement should not leave the selenium atoms in a chemically metastable form.

The retention

For both isomers the retention values are high and reach 100% for ^{81m}Se on slow neutron irradiations. The spread of the results does not allow a definite comparison with the earlier results. The isomeric effect cannot be vigorously demonstrated because of the high retention. It is indeed known that comparison of activity ratios in the *retained* and the *free* fraction makes isomeric effects more noticeable in the case of high retentions. But the low activity of free recoil selenium has not made this feasible.

The high retention values might be explained by the simplicity of the compound. Crystal rearrangements are of course more readily obtained in less complicated compounds. Thermal and radiation annealing during and after irradiation are in these cases very effective.

The slight differences between samples bombarded with (α,n) and (d,n) neutrons might also be due to the different radiation damage created in the crystals. This disturbing influence, together with the low amounts of recoil selenium, has made it impossible to throw more light on the influence of the neutron energy on the isomeric effect.

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The mass spectrometry of isocyanic acid

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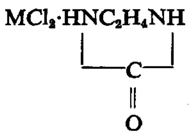
Since urea can co-ordinate either through one of its nitrogens or through the carbonyl oxygen, a thermal decomposition study of cyclic urea–metal complexes of the type



$$\mathrm{MCl_2\cdot HNC_2H_4NH}\quad(\mathrm{HN}\text{—}\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}\text{—}\mathrm{NH})$$

has been undertaken to determine if and how the decomposition characteristics change when the metal–ligand bond changes.(1) The decompositions have been studied by static and dynamic

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(1) S. R. Smith, H. B. Jonassen and R. E. Berni, to be submitted to *J. inorg. nucl. Chem.* 1967.

techniques and decomposition products have been analyzed by mass spectrometry. Identification of the products has been accomplished by a study of the mass spectra. Difficulty was encountered in the assignment of the mass 43 peak and in attempts to correlate this peak in the static and dynamic runs. HNCO was considered a reasonable assignment for this peak and its behaviour indicated the advisability of a separate study of the mass spectrometry of isocyanic acid.

EXPERIMENTAL

Preparation of isocyanic acid

Two methods were used for the preparation of isocyanic acid:

Depolymerization of cyanuric acid.[2] Cyanuric acid (Eastman-Kodak White Label) was heated at 450°C on the inlet system of a C.E.C. 21-614 residual gas analyzer modified to serve as an analytical mass spectrometer. At this temperature about 3 per cent of CO_2 and a very small amount of HCN and a trace of water were present as impurities. At temperatures between 450° and 500°C the amount of CO_2 formed in the depolymerization increased very markedly.

Reaction of KNCO[3] *and* $KHSO_4$. This reaction produced a large amount of CO_2 at all temperatures. A cold trap purification had to be effected before the HNCO could be analysed mass spectrometrically.

Mass spectrometer studies

Upon preparation about 150 μ of HNCO was expanded into the expansion volume of the C.E.C. 21-614 mass spectrometer. The mass spectrum was recorded immediately after preparation.

TABLE 1.—MASS SPECTRUM OF HNCO

Mass	Relative intensity	Mass	Relative intensity
12	4·39	26	3·51
13	0·35	27	3·53
13·5	0·03	28	4·08
14	3·35	29	17·77
15	13·49	30	2·04
16	0·94		
17	0·09	42	22·77
21	0·21	43	100·00
21·5	1·83	44	1·56
22	0·02	45	0·10

After the mass spectrum was scanned the HNCO sample was isolated in the expansion volume and rerun at intervals for approx. 1 week. The presence of HCN in the stored HNCO sample obtained from the cyanuric acid depolymerization was differentiated by the slower rate of decay of the peaks associated with HCN compared to those of HNCO. The spectrum of HNCO corrected for impurities is shown in Table 1, it is essentially the same as that obtained by RUTH and PHILIPPE.[2]

RESULTS AND DISCUSSION

The logarithm of the intensity of the mass peak 43 is plotted against time in Fig. 1. The disappearance of HNCO in storage follows a first-order rate law. The half life of this polymerization reaction to cyanuric acid is 18·0 hr at 30°C.

The significance of this polymerization in the analytical chemistry of stored gas samples containing HNCO is obvious.

YOST and coworkers[4] have indicated that in the vapour this molecule is present predominantly if not exclusively as HNCO.

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[2] J. M. RUTH and R. J. PHILLIPE, *Analyt. Chem.* **38**, 720 (1966).

[3] *Inorg. Synth.* (Edited by W. C. FERNELIUS), Vol. II, p. 87. McGraw-Hill, New York (1956).

[4] L. H. JONES, J. H. SHOOLERY, R. G. SHULMAN and D. M. YOST, *J. chem. Phys.* **18**, 990 (1950).

Examination of the mass spectrum indicates the presence of intense ions at mass 15 (NH^+) and at mass 29 (COH^+). Under electron impact there is the probability of a transfer of the hydrogen from the nitrogen atom.

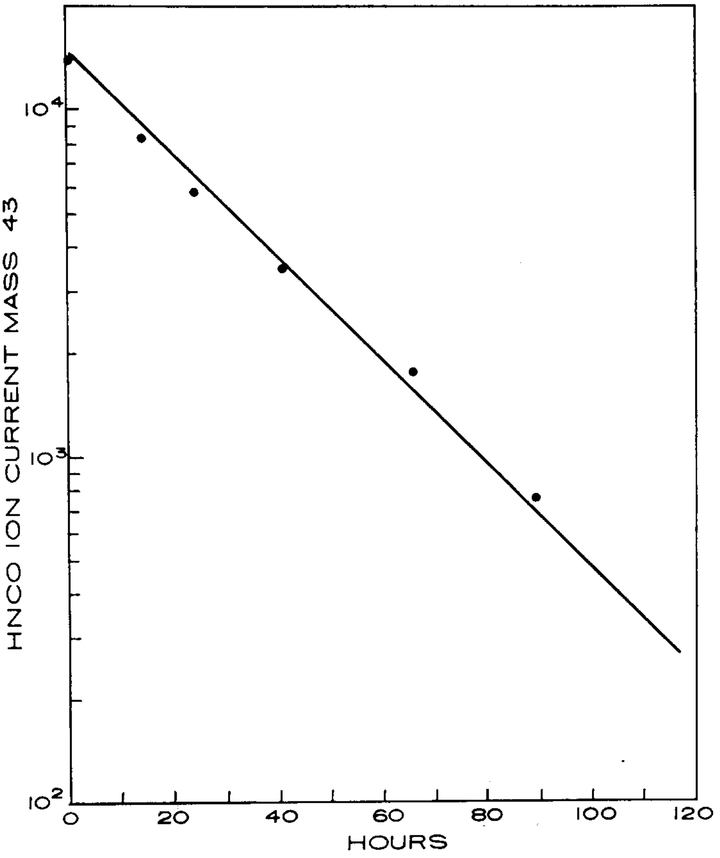

Fig. 1.

Furthermore, the presence of ions of the type CH^+ (M13), OH^+ (M17), NO^+ (M30) indicates the possibility of a triangular structure of the ion in the transition state prior to the decomposition that gives rise to the ions observed in the spectrum.

The study of the kinetics of the polymerization of HNCO by direct mass spectrometer method is in progress.

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