DECOMPOSITION OF METHYL ISOTHIOCYANATE IN AQUEOUS SOLUTION

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In neutral aqueous solution, methyl isothiocyanate, CH₃NCS, has been found to decompose at significant rates with the formation of N-methyldithiocarbamate (1) and 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione (2). Thus, at room temperature, $0\cdot 1 \mod dm^{-3}$ solutions of methyl isothiocyanate deposited yellow crystals (m.p. $105-110^{\circ}$) after c. 1 month. On recrystallization, fine white needles of (2) (m.p. 122- $122 \cdot 5^{\circ}$) were collected. The dithiocarbamate (1) is a probable intermediate in the formation of (2), since its concentration, initially very low, rises to detectable levels in a few days, reaches a maximum value about 5% of the initial methyl isothiocyanate concentration, and then slowly declines to reach undetectable levels after several months. In alkaline dioxan-water solutions it has been reported¹ that alkylmonothiocarbamates are formed, but we have been unable to detect this product.



The formation of N-methyldithiocarbamate involves catalysis by trace metals, notably copper. Thus, in ordinary laboratory distilled water, as much as 20% reaction was observed per month, but much less in redistilled water, and virtually none in the presence of low concentrations (e.g. $10^{-4} \text{ mol dm}^{-3}$) of EDTA. Further reaction to give (2) is apparently due to oxidation of (1) by dissolved oxygen. No (2) was detected when oxygen was excluded, and the rate of formation appears to depend on the partial pressure of oxygen. Conditions which stopped the formation of (1) also stopped the formation of (2) from methyl isothiocyanate. The reactions involved thus appear to be:

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¹ Zahradnik, R., Colln Czech. chem. Commun., 1959, 24, 3407.

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Experimental

Preparations

Methyl isothiocyanate (B.D.H. laboratory grade) was distilled twice before use.

Standard methods were used for the preparation of the other compounds, i.e. sodium N-methyldithiocarbamate² and 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione.² For the latter process, the claimed² product is 4-methyl-3-methylimino-1,2,4-dithiazolidine-5-thione (3) (m.p. 86°), but this seems inconsistent with the method reputedly used in its isolation (which should have led³ to isomerization to (2)). Our product transformed into (3) by the known reaction sequence.³

Identification of Reaction Products

N-Methyldithiocarbamate.—The presence of this substance was detected by the use of an absorption peak at 284 nm which is replaced by another at 360 nm on addition of copper(II). Quantitative estimation was possible by determining the amount of copper(II) which just caused removal of the 284 nm peak. From measurements on an authentic sample of sodium N-methyl-dithiocarbamate, the absorption coefficient was established as $1 \cdot 2 \times 10^4$ cm dm³ mol⁻¹ at 284 nm. Using this value, estimations of the concentration of (2) in the decomposing methyl isothiocyanate solutions were made. These were within 15% of those determined by the copper(II) method above.

All solutions of the copper complex behaved identically, with slow fading of the yellow coloration. N-Monoalkyldithiocarbamates are known⁴ to reduce copper(II) slowly to copper(I). This prevented isolation of the solid copper(II)–N-methyldithiocarbamate complex.³ Also, after extensive exposure to the air, authentic solutions of (1) slowly precipitated a yellow material which was identified as crude (2).

A sample of methylmonothiocarbamate, prepared by an established method,⁵ showed an absorption peak at 226 nm, in good agreement with previous measurement.⁵ It was verified that the presence of more than a very few per cent of this product would have been detected if present.

2,4-Dimethyl-1,2,4-thiadiazolidine-3,5-dithione.—Recrystallization of the crude product from hot water gave colourless needles, m.p. $122-122 \cdot 5^{\circ}$ (Found: C, $27 \cdot 0$; H, $3 \cdot 5$; N, $15 \cdot 2$; S, $52 \cdot 4$. C₄H₆N₂S₃ requires C, $27 \cdot 0$; H, $3 \cdot 4$; N, $15 \cdot 7$; S, $53 \cdot 9\%$). Mass spectroscopy (molecular weight 178), and the n.m.r. spectrum in D₂O (two non-identical, non-adjacent methyl groups) confirmed that the material was (2). Both the crude yellow product and the recrystallized material gave infrared spectra which could not be distinguished from the spectrum of an authentic sample.

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- ³ Bradsher, C. K., Brown, F. C., Sinclair, E. F., and Webster, S. T., J. Am. chem. Soc., 1958, **80**, 414.
- ⁴ Thorn, G. D., and Ludwig, R. A., "The Dithiocarbamates and Related Compounds." p. 61. (Elsevier: Amsterdam 1962.)
- ⁵ Svatek, E., Zahradnik, R., and Kjaer, A., Acta chem. scand., 1959, 13, 442.