Radiation Induced Conversion of Ammonium Thiocyanate to Thiourea

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It is well known[1,2] that isomerisation of ammonium thiocyanate to thiourea takes place at temperatures above its mp, attaining a steady state after 1 hr, corresponding to 25 per cent conversion. A study has now been carried out on the effect of UV and γ-radiations on this system at various temperatures, in an attempt to arrest the back reaction and increase the yield of thiourea.

Accurately weighed quantities of A. R. ammonium thiocyanate (2 g) were taken in 15 mm × 100 mm pyrex tubes and sealed. These were irradiated with a 1000 curie Co-60, γ-source (γ-cell 220, AEEC, Canada) to various doses (dose rate 7.271×10^{16} eV/g/min) and temperatures. The irradiations at various temperatures were carried out for one hour(8.7×10^{18} eV/g). For experiments in UV, a Hanovia XI arc lamp was used (7.8×10^{19} quanta at 2537 Å), placing the samples in an open dish at 10 cms distance. After irradiations the sample was dissolved in a little water, made upto 1000 m*l* and the UV spectra taken at 245 mμ as described earlier.[3] Using the following expression

$$\% \text{ Conversion} = \frac{\text{O.D.}_{\text{observed}} - 0.1845\,A}{0.1564\,A}$$

(where A was the amount of ammonium thiocyanate taken) the yields were calculated.

It is seen from Fig. 1, that the yields of thiourea are appreciable under γ-irradiation. Thus, at 130 and 140°C the amounts of thiourea formed are 4.5% and 12.5% respectively (the conversion due to heat alone being nil and 1% at these temperatures). The maximum conversion obtained by keeping the samples for one hour at 170°C, is

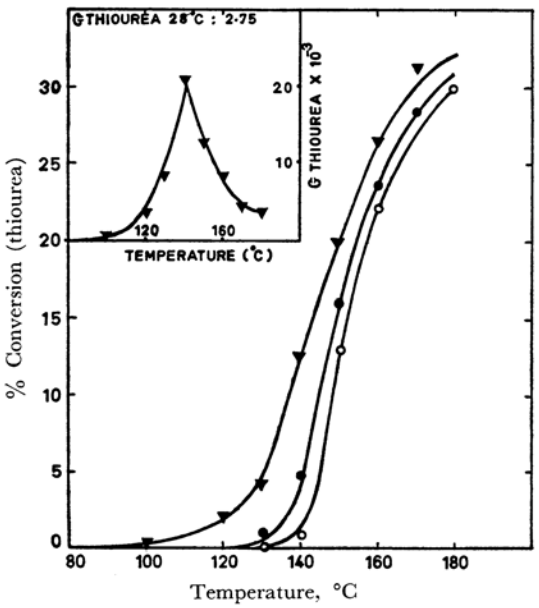

Fig. 1. Radiation induced conversion of ammonium thiocyanate to thiourea at various temperatures.
Dose 4.36×10^{18} eV/g
○—○ heat alone
●—● heat + hν
▼—▼ heat + γ-rays

28.79% with heat and 31.43% with γ-radiations.

A set of representatives curves for the effect of temperature and γ-radiations at various temperatures are presented in Fig. 2.

Influence of Temperature Alone. The conversion to thiourea is (1) linear in the range 140—170°C with time of heating upto 30 min; (2) above 170°C the saturation that sets in can be attributed to (a) the reversible back reaction thiourea-thiocyanate taking place and also (b) the decomposition of thiourea in air resulting in liberation of H_2S.

1) A. I. Vogel, "A Text Book of Practical Organic Chemistry," 3rd Ed (1961), p. 442.
2) Hai-han Hsu and Han-Chang-wang, *Hue Hsueh Hsueh Pao*, **30**, 363 (1964); *Chem. Abstr.*, **61**, 15399.
3) S. T. Talreja, P. M. Oza, and P. S. Rao, *Anal. Chim. Acta*, **36**, 238 (1966).

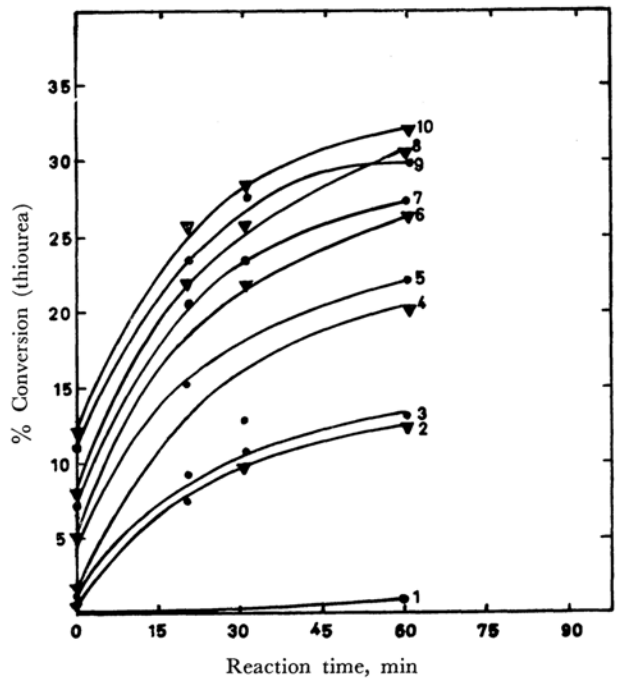

Fig. 2. Reaction time *vs.* % conversion (thiourea) curves at various temperatures, and dose rate being 7.271×10^{16} eV/g/min.

1. 140°C 2. 140°C+γ 3. 150°C 4. 150°C+γ 5. 160°C 6. 160°C+γ
7. 170°C 8. 170°C+γ 9. 180°C 10. 180°C+γ

γ-Irradiations. It has been observed that very high doses (5×10^{22} eV/g) are required for any conversion to detectable amounts of thiourea at room temperature (28°C) the G value obtained being 2.75. However, as the temperature is increased the G_{thio} rises rapidly to 3649 at 120°C and to a maximum at 140°C, the value being 20980 (*inset,* Fig. 1). It decreases steadily there after. Part of the diminution in the yield can be attributed to pyrolysis of thiourea, leading to gaseous products like H_2S and part to radiation decomposition of thiourea.

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