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INVERSION OF THE CYANIDE GROUP
INTO ISO-CYANIDE UNDER GAMMA IRRADIATION

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A B S T R A C T

Infrared spectrophotometric evidence indicates that gamma irradiation of the nitriles causes partial inversion of the cyanide group into iso-cyanide according to the following mechanism: In the gamma flux, some of the cyanide groups are detached from the nitrile as cyan free radicals and, owing to their resonance-hybrid structure, $\cdot\text{C}\equiv\text{N} \leftrightarrow \text{C}\equiv\text{N}\cdot$, two distinct recombination processes take place leading partly to the usual cyanide and partly to the iso-cyanide, respectively. From a comparison of the optical densities at the characteristic frequency of the iso-cyanide absorption band in irradiated methacrylonitrile and ethyl iso-cyanide it is concluded that at least 20% of the cyanide groups were transformed into iso-cyanide in a specific sample of methacrylonitrile irradiated to a total dose of 0.1 megarads.

During a study of the γ -ray initiated polymerization of methacrylonitrile in bulk, infrared spectrophotometric examination of the polymerizing system showed the appearance of two peaks at 2010 and 2090 cm^{-1} , respectively. The first peak, which increased regularly with the gamma dose corresponds to ketenimine linkages identified previously¹ in radical-initiated polymerization of the same monomer, and will be discussed elsewhere.

We assign the peak at 2090 cm^{-1} (Fig. 1) to the iso-cyanide group formed via inversion of the cyanide group according to the following mechanism: Under γ -irradiation .CN free-radicals are detached from the nitrile and, owing to their resonance-hybrid structure, $\cdot\text{C}\equiv\text{N} \leftrightarrow \text{C}\equiv\text{N}\cdot$, two distinct recombination processes take place, leading partly to the usual cyanide and partly to the iso-cyanide, respectively.

This assignment and the mechanism proposed are supported by the following observations:

- (1) A weak band has been reported practically at the same frequency (2100 cm^{-1}) and attributed to N-C stretching of the iso-cyanide^{2,3,4} in iso-cyanosilanes.
- (2) Ethyl iso-cyanide was synthesized from silver cyanide and ethyl iodide (sealed tube, 100-110°C, 19 hours, fractional distillation). A band was obtained, practically at the same frequency (Fig. 1, lowest dotted curve).

(3) HCN has been detected⁵ in the gases formed during γ -irradiation of solid polymethacrylonitrile. This proves definitely that .CN free-radicals do form under irradiation.

(4) The peak in question is not found in the spectrum of the irradiated solid polymer, even after cumulative doses as high as several hundreds of megarads; it is observed only in the liquid polymerizing system, in agreement with the small size and, consequently, high escaping ability of the .CN radicals: In the liquid phase they are trapped by other radicals, whereas in the irradiation of the finished polymer their trapping is highly improbable.

(5) The simplest alkyl cyanide, acetonitrile (Fluka, purum), was taken and its spectrum recorded (after NaOH washings). The spectrum showed a peak at 2070 cm^{-1} (Fig. 2a, solid curve), which cannot be attributed to CH_3NC which might be contained in the original material, because it persisted in fractional distillation. The spectrum of the very first fraction (about 1/100) was examined, and a new peak was found at 2090 cm^{-1} (Fig. 2a, dashed curve).

(6) Crude acetonitrile was hydrolyzed with diluted sulfuric acid. If some iso-cyanide were present, formic acid would distill over, which must reduce an ammonia solution of silver hydroxide: This has actually occurred.

(7) Acetonitrile, whose spectrum is shown in Fig. 2a (solid curve), was irradiated near the core of TR-1. Its spectrum after a pure gamma dose of 8 megarads is shown in Fig. 2b; here again a new peak appeared at 2090 cm^{-1} . Since the peak was very weak, its significance was

checked by using higher amplification (5X). The resulting spectrogram is reproduced in Fig. 2b (solid curve). Although the gamma-ray polymerization of acetonitrile has been investigated extensively by infrared spectrometry⁶, a peak at this frequency has not been reported.

(8) The spectrum of irradiated methacrylonitrile was also taken under the same conditions (Fig. 1). A comparison shows that the peaks that appear upon gamma irradiation both in methacrylonitrile and in acetonitrile have the same frequency. Furthermore, the new peak observed in the head-fraction from the fractionation of crude acetonitrile is indistinguishable from the one originating from γ -irradiation.

(9) It is interesting to note that an extremely weak but significant peak can also be seen exactly at the same position in the spectrum of unirradiated crude methacrylonitrile (Fig. 1, upper solid curve).

C O N C L U S I O N

From the arguments presented above we conclude: (1) That γ -irradiation of nitriles causes partial inversion of the cyanide group into iso-cyanide, and (2) That, unless vigorously purified, the nitriles usually contain small amounts of iso-nitriles. The presence of the latter could, presumably, be explained by the formation of .CN free-radicals through partial pyrolysis of the product nitrile during dehydration of the corresponding amide by P_2O_5 . Rather high temperatures are, of course, conceivable to set up on the surface of the reaction vessel in which the heterogeneous solid

mixture is heated. (3) In irradiated methacrylonitrile optical densities of the iso-cyanide group were observed which were as high as 20% of the optical density of the same group in ethyl iso-cyanide. Assuming that the molar extinction is roughly the same in both cases, one can estimate the fraction of the cyanide groups of methacrylonitrile which transform into iso-cyanide to be at least 20% in a specific sample irradiated to a total gamma dose of 0.1 megarads.

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FIGURE CAPTIONS

Fig. 1. Infrared spectra of methacrylonitrile (MAN) and ethyl iso-cyanide (EIC). Upper solid curve: Unirradiated MAN (Fluka, purum); dashed curve: Irradiated MAN (6 M.rads); lower solid curve: The same as the latter, 5X amplified. Lowest dotted curve: EIC (The transmittance % values were shifted 55 units downward for clarity). (Perkin-Elmer 221, 0.1 mm. cell thickness.)

Fig. 2. Infrared spectrum of acetonitrile. (a) Solid curve: Unirradiated (Fluka, purum); dashed curve: Head-fraction from distillation of the unirradiated sample. (b) Irradiated acetonitrile (8 M.rads); the same spectrum is shown with two different amplifications to prove the significance of the very weak peak observed. Dashed curve: 1X; solid curve: 5X. The (a) curves were shifted 10 transmittance % units upward for clarity.

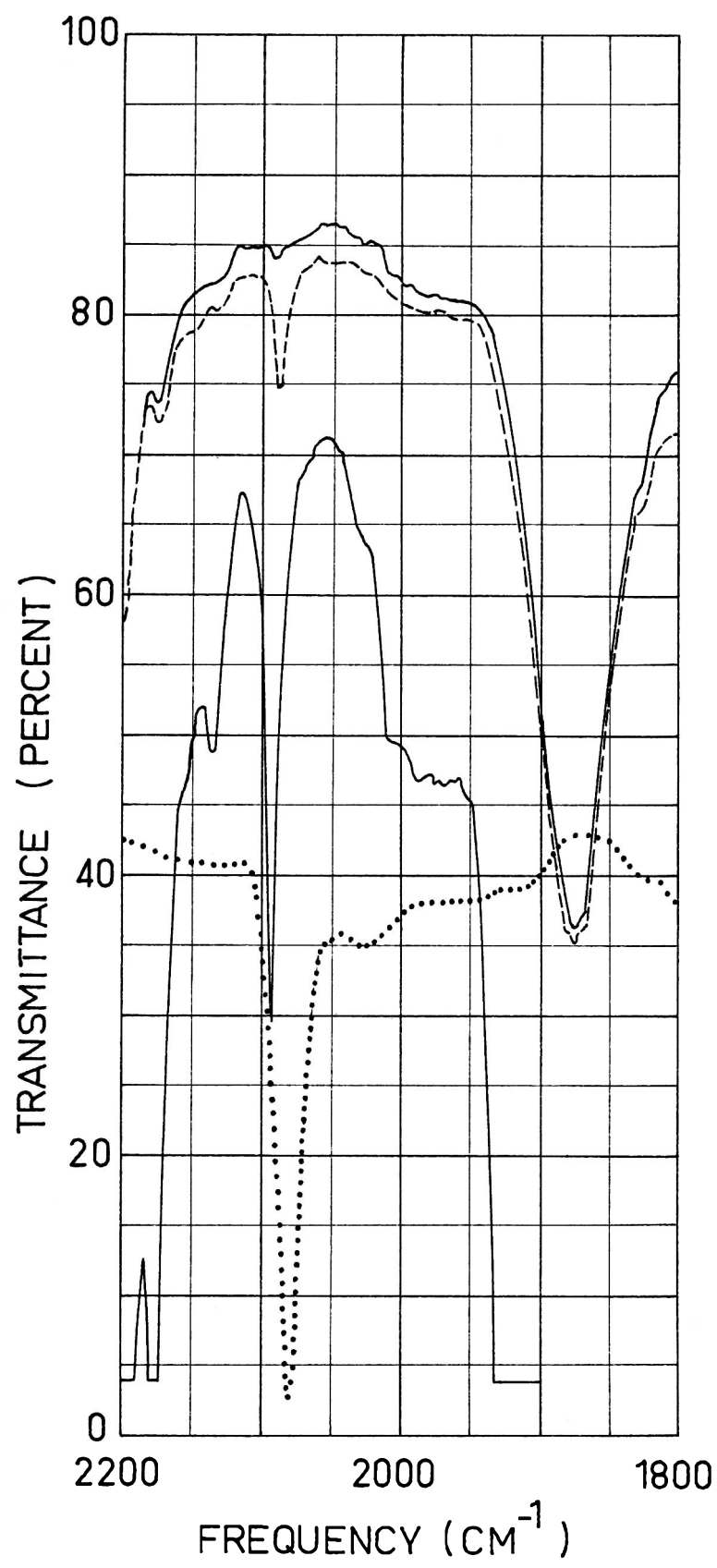


Fig. 1

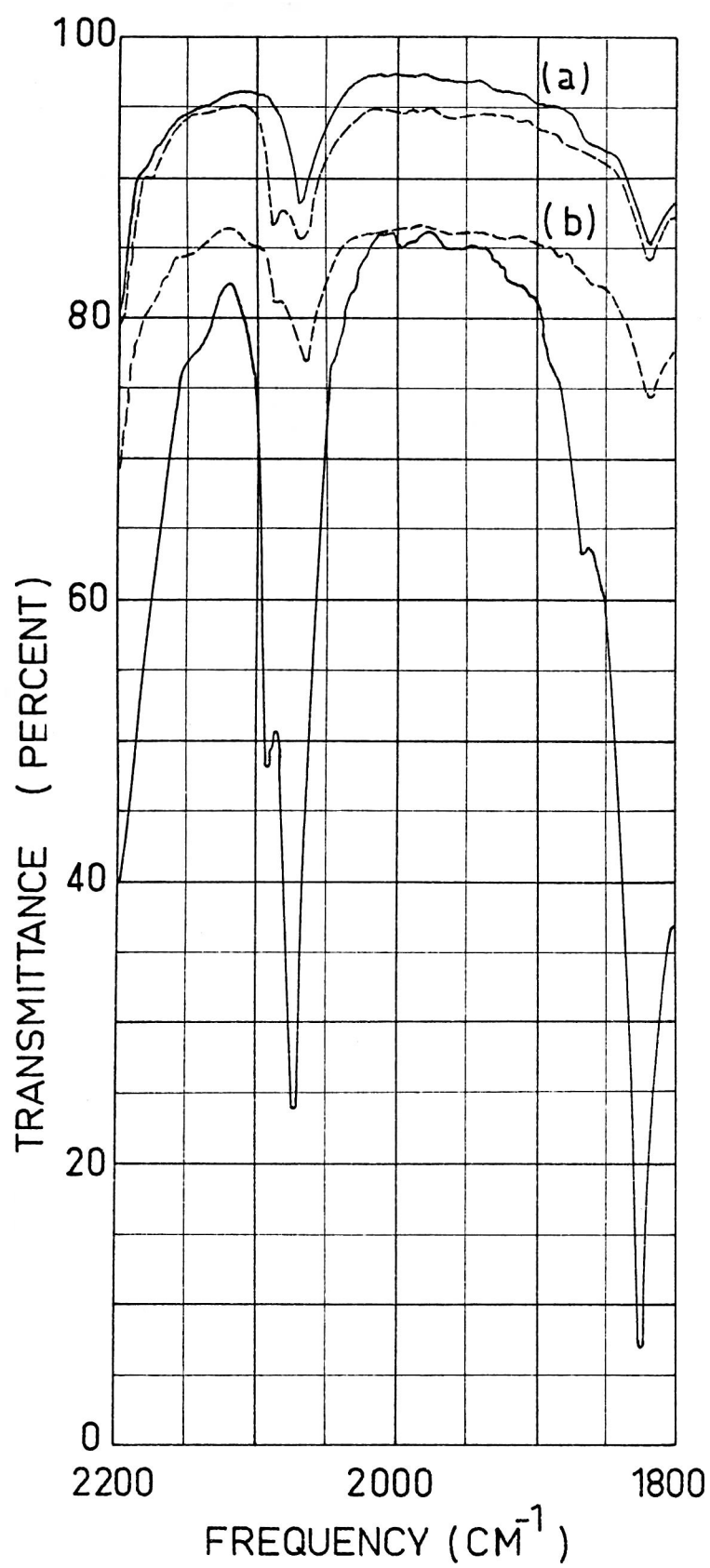


Fig. 2