

From the results obtained at an incident dosage of  $1.21 \times 10^{18}$  nVt (thermal) (Table 1) and those obtained at  $0.76 \times 10^{18}$  nVt (thermal) it follows that *p*-xylene polymerizes according to the same rate law as biphenyl, which means that the reaction is a first-order process<sup>1</sup>.

Mixtures of *p*-xylene and biphenyl varying in composition from 4.75 to 28.5 per cent weight of *p*-xylene were irradiated under the same conditions. The experimental results show that within the limit of accuracy of the analytical method the first-order rate law also applies. The results for heavy tar formation are not so conclusive as those concerning the *p*-xylene/biphenyl ratio. The rather large scatter of the results about heavy tar content versus *p*-xylene/biphenyl ratio may be attributed to the limitations of the analytical method used. The general trend of the results is, however, in agreement with a first-order rate law.

From the similarity of behaviour of *p*-xylene and biphenyl under the influence of mixed pile radiation one may also expect a similar behaviour with respect to gamma irradiation. As regards the radiochemical polymerization yield  $G_p = \frac{\text{molecules polymerized}}{100 \text{ eV.}}$  of *p*-xylene, its magnitude may be taken as approximately 1.45 times the corresponding value for biphenyl.

A more detailed account will be published elsewhere.

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### Use of Ionizing Radiation in Spot Tests for Nitrogenous Compounds

SEVERAL spot tests are available for determining substances containing nitrogen, and are widely used in qualitative and semi-quantitative analysis<sup>1</sup>. All these involve the development of colour or fluorescence by spraying with suitable reagents. We have discovered that many nitrogenous compounds give a brown colour when spotted on to filter paper and exposed to doses of ionizing radiation in the range  $5 \times 10^6$ – $2 \times 10^8$  rads.

The results described below stem from an observation by one of us that ammonium dihydrogen phosphate spotted on filter paper and exposed to a flux of  $10^{13}$  neutrons/cm.<sup>2</sup>/sec. in the reactor *Bepo* for six days developed a brown colour. In subsequent work we used a 4-MeV. linear accelerator as a radiation source, since this could be used to deliver  $10^8$  rads in a much shorter time than the reactor and without inducing any radioactivity. Several different types of filter paper were tested and Whatman No. 4 selected as the most suitable: all papers became brittle and pale yellow after  $10^8$  rads, and cellulose acetate papers crumbled completely away after this treatment<sup>2</sup>. Colours developed slowly at room temperature and faster on warming. The best con-

ditions for colour development were obtained using aliquots containing about 20  $\mu$ gm. nitrogen exposed to  $10^8$  rads, when the limit of detection was approximately 2  $\mu$ gm. nitrogen. Under these conditions well-defined brown spots were obtained from the following materials: ammonium chloride, methylamine hydrochloride, diethylamine hydrochloride, glycine, alanine, asparagine, proline, potassium nitrate, sodium nitrite and nitrobenzene. Fainter spots were obtained with acetamide, diphenylamine, pyridine and azobenzene, but no spots could be found when tetramethyl ammonium bromide and cetyl trimethyl ammonium bromide were tested.  $\beta$ -indolyl acetic acid gave a pink spot, while aspartic acid and trimethylamine hydrochloride were anomalous in giving deep brown spots on heating (with or without ionizing radiation).

The colour formation is probably due to a Maillard reaction between amino-groups and aldehydic substances resulting from radiation-induced breakdown of cellulose. Presumably nitro groups are reduced to amino groups under these conditions of irradiation, and tertiary amines like pyridine undergo ring cleavage. However, no improvement in colour development could be obtained by soaking the filter paper in glucose solution before spotting and irradiating. As an analytical technique, the reaction is not so sensitive as the ninhydrin reaction for amino-acids, which can detect about 0.1  $\mu$ gm. nitrogen, but it might be useful for detecting other substances which do not give the ninhydrin test. It has been used to develop paper chromatograms of amino-acids.

Finally, the reaction may be of interest to those concerned with radiation dosimetry. The fact that a colour will develop at  $5 \times 10^6$  rads, which is near the sterilizing dose for food and pharmaceutical materials, is important in this connexion.

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<sup>1</sup> Feigl, F., "Spot Tests in Organic Analysis" (Elsevier, 1956).

<sup>2</sup> Saeman, J. F., Millett, M. A., and Lawton, E. J., *Indust. Eng. Chem.*, **44**, 2848 (1954).

### Radiation Synthesis of Urea

LOISELEUR and PETIT<sup>1</sup> have reported that urea is formed in the X-irradiation of an ammoniacal and methanolic solution of *m*-phenylenediamine and dichloromethane in the presence of air. A further report has been given recently by Loiseleur, Petit and Clémentin<sup>2</sup> on the effect of oxygen-acceptors on the yield of urea. We set out to synthesize substituted ureas and to study the proposed mechanisms, but we found that no urea was formed in experiments with similar solutions.

$\gamma$ -radiation from a caesium-137 source (dose-rate:  $10^{18}$  eV./ml./min.), taking  $G_{Fe^{3+}} = 15.5$ , and X-rays from a copper target at 40 kV. and 20 m.amp. (dose rate:  $1.5 \times 10^{15}$  eV./ml./min.) were used in the experiments. Closed glass irradiation cells of 25 ml. capacity were fitted with polythene capillary tubing through which air was bubbled, after it had first passed through a vessel containing the solution to be irradiated. The solution (32 ml. methanol, 4 ml. dichloromethane, 250 mgm. *m*-phenylenediamine,