Radiation-induced Nitration of Benzene

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A NOVEL, high-yield method of preparing nitrobenzene from liquid benzene and nitrate salts uses *X*-ray irradiation to induce the reaction. Little work has been done with metallic nitrates as nitrating reagents.[1]

A heterogeneous mixture of anhydrous potassium nitrate (50 g.) and benzene (22 g.) sealed in a General Electric liquid-sample cell, with exclusion of air, was irradiated (G.E. XRD-5-*X*-ray unit; Machelett tungsten target–beryllium window *X*-ray tube; 50 kv., 30 mA) for varying lengths of time. Conversions as high as 95% were obtained when the mixture was agitated. The characteristic odour of nitrobenzene was apparent on opening of the cell. Its presence was confirmed by distillation of the product and comparison with known material. A plot of chemical yield (obtained by integrating g.l.c. traces of the benzene remaining and the nitrobenzene formed) against time is shown in the Figure. Titration of the hydroxide formed with N-hydrochloric acid, confirmed the yields estimated from g.l.c., and established the stoicheiometry shown below:

$$PhH + KNO_3 \rightarrow PhNO_2 + KOH$$

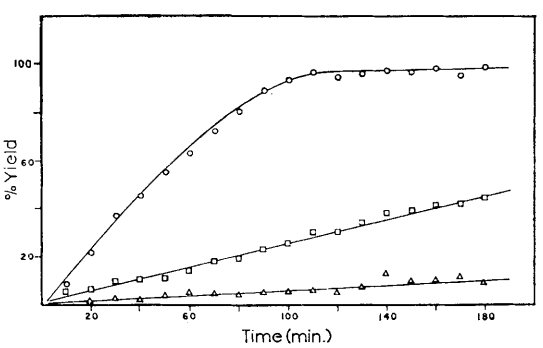

FIGURE. X-*Ray irradiation of* KNO_3 *in benzene.*
○—*Tungsten target: mixture stirred.*
□—*Tungsten target: mixture not stirred.*
△—*Cobalt target: mixture stirred.*

The high conversion into nitrobenzene is partly due to the fact that benzene and nitrobenzene are relatively stable to *X*-ray irradiation[2] so that further reactions do not take place to any great extent. In contrast to the normal nitrating procedure, no further nitration products could be detected even by g.l.c.

A number of variables, in addition to time of irradiation, was investigated. The effect of agitation can be seen from the Figure by comparing the stirred mixture with the non-agitated one. The low yields from the non-stirred mixture are presumably due to stratification. Similar curves were obtained by using anhydrous copper, sodium, and barium nitrates, indicating the unimportance of variations in the metal. The production of nitrobenzene apparently is wavelength dependent since exposure to radiation from a cobalt target at equivalent energy gave low yields (Figure).

The *G* value for the reaction was estimated to be 39, the *G* value for formation of hydrogen from benzene being used as a standard.[3] This high *G* value indicates either a chain reaction involving a chemically active propagating species or a highly efficient energy-transfer process.

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[1] It has been reported that nitrobenzene can be prepared by the reaction of benzene vapour with fused nitrate salts: R. B. Temple, C. Fay, and J. Williamson, *Chem. Comm.*, 1967, 966.

[2] J. Errera and V. Henri, *J. Phys. Radium*, 1926, **7**, 225; A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, Oxford, 1960.

[3] C. E. Klots and R. H. Johnsen, *J. Phys. Chem.*, 1963, **67**, 1615.