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THE FREE RADICAL DECOMPOSITION OF BENZOYL NITRATE AND ITS PRESSURE DEPENDENCE

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Abstract—The free radical decomposition of benzoyl nitrate in benzene and toluene to give products resulting from the formation of phenyl and benzoyloxy radicals is described. These products include biphenyl from reactions in benzene and benzyl benzoate and methylbiphenyls from reactions in toluene. The yields of radical decomposition products are comparable to yields of the non-radical decomposition products of benzoyl nitrate, benzoic anhydride and benzoic acid. The marked effect of applied pressure in inhibiting the radical mode of decomposition is also described.

INTRODUCTION

BENZOYL nitrate, an unstable liquid made at low temperature by reaction of benzoyl chloride with silver nitrate,[1] decomposes to form benzoic anhydride and oxides of nitrogen.[1] Its nitrating properties have been shown[2] to be due to fast nitration by dinitrogen pentoxide formed in the equilibrium in Eq. (1)

$$2PhCO{:}ONO_2 \rightleftharpoons (PhCO)_2O + N_2O_5 \qquad (1)$$

This compound has recently been postulated as an intermediate in high pressure reactions of carbon monoxide with phenylmercury (II) basic nitrate in benzene and toluene.[3] Products from these reactions include not only benzoic anhydride but products resulting from decomposition of an intermediate to give benzoyloxy and phenyl radicals. The radical decomposition of benzoyl nitrate and its inhibition by applied pressure have been demonstrated and are now described.

RESULTS

Benzoyl nitrate was made as a pale yellow liquid by reaction of benzoyl chloride with silver nitrate in carbon tetrachloride at −10° under dry conditions. It decomposed fairly rapidly on warming to room temperature, evolving brown fumes and leaving a residue of benzoic anhydride and benzoic acid. However, small samples could be rapidly examined by IR spectroscopy as liquid films between sodium chloride plates.

A dilute solution of the compound in benzene, heated under reflux, emitted brown fumes and was found to contain as major reaction products biphenyl and nitrobenzene as well as benzoic anhydride and benzoic acid. Repeating this experiment with a more concentrated solution gave, in addition to these products, phenyl benzoate and *m*-dinitrobenzene in significant quantities. When toluene was used as a solvent, good yields of the three isomeric methylbiphenyls (*o*, *m* and *p*) and benzyl benzoate were found among the reaction products after removal of benzoic acid. Nitro-products were present, but no biphenyl or bibenzyl. The authentic methylbiphenyls were prepared for comparison by heating under reflux a dilute solution of benzoyl peroxide in toluene. Bibenzyl was also produced in this reaction.

The reaction between benzoyl nitrate and benzene was unaffected by carrying out the refluxing under an atmosphere of nitrogen, but a pressure of 200 atmospheres of nitrogen had a marked effect on the reaction products obtained. These included nitrobenzene and *m*-dinitrobenzene as well as benzoic anhydride and benzoic acid, but no biphenyl or phenyl benzoate were present. The products of a reaction carried out under 190 atmospheres of carbon monoxide included some nitrobenzene, but no biphenyl, phenyl benzoate or *m*-dinitrobenzene.

DISCUSSION

The isolation of biphenyl and phenyl benzoate from reactions of benzoyl nitrate with benzene indicates radical decomposition to form benzoyloxy radicals, which then decarboxylate to form phenyl radicals (Eqs (2) and (3)).

$$\mathrm{PhCO \cdot ONO_2 \rightarrow PhCO_2^{\bullet} + NO_2} \tag{2}$$

$$\mathrm{PhCO_2^{\bullet} \rightarrow Ph^{\bullet} + CO_2} \tag{3}$$

Phenylation and benzoyloxylation of the benzene then occurs, as with benzoyl peroxide.[4] The reactions with toluene confirm the formation of these radicals but the formation of benzyl benzoate instead of the bibenzyl formed in a reaction of benzoyl peroxide with toluene (at an approximately similar concentration) suggests that coupling of benzyl and benzoyloxy radicals (Eqs (4) and (5)) occurs instead of dimerization of benzyl radicals. This suggests a slower decomposition in the case of benzoyl nitrate.

$$\mathrm{R^{\bullet} + PhCH_3 \rightarrow RH + PhCH_2^{\bullet}} \tag{4}$$

$$(\text{where } \mathrm{R = Ph} \text{ or } \mathrm{PhCO_2})$$

$$\mathrm{PhCH_2^{\bullet} + PhCO_2^{\bullet} \rightarrow PhCH_2OCOPh} \tag{5}$$

The suppression of the radical decomposition by an applied gas pressure is consistent with observations in the reactions of phenylmercury (II) basic nitrate with carbon monoxide in benzene,[3] in which radical decomposition products progressively replace benzoic anhydride as the gas pressure employed is lowered. The radical decomposition of benzoyl peroxide is also retarded by applied pressure,[5] but in the case of benzoyl nitrate the more marked effect of increased pressure may be due to its effect of promoting the alternative mode of decomposition, to give benzoic anhydride. This decomposition presumably occurs by a polar bimolecular mechanism, which is likely to be favoured by applied pressure through association of solvent molecules with an intermediate.[6]

A high pressure of carbon monoxide apparently has the additional effect of reducing the amount of nitro-products formed. This is presumably due to reduction of nitrating species such as oxides of nitrogen by carbon monoxide.[7] The reduction of nitric acid in benzene by high pressure of carbon monoxide has been demonstrated.[3] A combination of both effects is thus responsible for the comparatively clean nature of reactions between phenylmercury (II) basic nitrate and carbon monoxide in benzene at gas pressures above 200 atmospheres.[3]

EXPERIMENTAL

Reactions of benzoyl nitrate with benzene. The solns of reaction products were evaporated and the residual sticky yellow solids examined by IR spectroscopy as thin films. These residues were then dissolved in CCl_4 which was shaken with 0·1N NaOH to extract benzoic acid. The organic phase was separated, washed with water, dried over $MgSO_4$, filtered and evaporated. The residues were then examined by IR spectroscopy and GLC. Biphenyl, phenyl benzoate, nitrobenzene and *m*-dinitrobenzene were all identified by comparison of their GLC retention times with authentic specimens, and all except nitrobenzene were collected off the column and identified by comparison of their IR spectra with authentic specimens.

IR spectra were run as liquid films or Nujol mulls on a Perkin–Elmer 137 Infracord Spectrophotometer. GLC analyses were carried out on a Perkin–Elmer 451 Fractometer using a 2 m × 0·6 cm packed column, with an LB-550-X (polypropylene glycol) stationary phase on Chromosorb W support. H_2 was the carrier gas, and the temps were 175–190°.

Benzoyl nitrate (0·9 ml) was dissolved in benzene (100 ml) and the soln, which turned yellow on heating, was heated under reflux for 4 hr. Brown fumes were emitted. After this time the soln was allowed to cool and treated as above. Examination of the crude reaction products by IR spectroscopy indicated the presence of benzoic acid and benzoic anhydride as well as large quantities of other products whose absorptions indicated monosubstituted benzene rings. Examination of the neutral products by GLC at 190° enabled biphenyl and nitrobenzene to be identified as the principal products other than benxoic anhydride.

An exactly similar reaction using benzoyl nitrate (1·1 ml) in benzene (60 ml) and a reflux time of $\frac{3}{4}$ hr afforded as neutral products nitrobenzene, *m*-dinitrobenzene, biphenyl and phenyl benzoate as well as benzoic anhydride.

A soln of benzoyl nitrate (1·0 ml) in benzene (50 ml), refluxed under N_2 for $\frac{3}{4}$ hr, was found to contain as the major neutral products nitrobenzene, biphenyl and phenyl benzoate as well as benzoic anhydride.

15 ml of a soln of benzoyl nitrate (1·1 ml) in benzene (refluxed over mercury (II) acetate: 60 ml) was loaded into a glass liner in a stainless steel autoclave. After fluxing, N_2 gas was pumped in to a press of 157 atm. The autoclave was then heated to 100° and the working conditions of 200 atm and 100° maintained for 3 hr. The soln of reaction products was treated as above and found to contain nitrobenzene and *m*-dinitrobenzene, but no biphenyl or phenyl benzoate.

A press reaction was carried out as above using benzoyl nitrate (0·55 ml) in benzene (refluxed over mercury (II) acetate: 30 ml), and CO gas. The working conditions of 190 atm and 100° were maintained for 3 hr. The soln of reaction products was treated as above, but although GLC examination at 190° indicated the presence of nitrobenzene, no biphenyl, phenyl benzoate or *m*-dinitrobenzene were present.

Reaction of benzoyl nitrate with toluene. Benzoyl nitrate (1·0 ml) was dissolved in toluene (50 ml) and the soln heated under reflux for 3 hr. The soln turned yellow and brown fumes were evolved. The soln was then treated in the same way as the benzene solns above and the principal neutral products (examined by GLC at 190°) other than benzoic anhydride were the 3 isomeric methylbiphenyls and benzyl benzoate, identified by IR spectra and GLC retention time in the same way.

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