PERKIN 2 COMMUNICATION

The efficacy of 'Claycop' in the dinitration of toluene

N. Llewellyn Lancaster, Roy B. Moodie* and John P. B. Sandall

Department of Chemistry, University of Exeter, Exeter, UK EX4 4QD

Claycop and acetic anhydride in tetrachloromethane are modestly catalytic and regioselective in the mononitration of toluene, but are neither catalytic nor regioselective in the nitration of 2-nitrotoluene.

The importance of regioselectivity in mononitration of reactive aromatics and the relative success of recent methods using solid supports have been recently summarised.[1] One such procedure, using 'Claycop' (montmorillonite clay impregnated with copper nitrate) with acetic anhydride (and if necessary nitric acid) in tetrachloromethane, has been reported to improve both yields and selectivities not only in mono-, but also in poly-nitration of aromatic compounds, relative to the same reactions carried out under homogeneous conditions.[2] As a prelude to a study of the use of this reagent for polynitration of heteroaromatics, we reinvestigated the dinitration of toluene. In order to show whether or not the reaction rate was enhanced by the presence of claycop the progress of the reaction with time was investigated. Samples were taken at time intervals, quenched and analysed by GC.

Fig. 1 shows the results for a reaction mixture prepared as described[2] and reported to give a 95% yield of 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) in a molar ratio of 6.6:1 in 4 h. It is clear that under the conditions toluene is rapidly converted into a mixture of mononitrotoluenes. (3-Nitrotoluene, not shown, was 4% of the early reaction mixture; separate studies showed that its further nitration was relatively slow and the products did not interfere with the analyses reported.) Subsequent conversions (Fig. 1) of 2-nitrotoluene into a mixture of 2,4-DNT and 2,6-DNT and of 4-nitrotoluene into 2,4-DNT follow a first-order course (rate constant ratio for the two processes was *ca.* 2.5:1) and dinitration is almost complete in 4 h.

Since our main interest was in the facilitation or otherwise by claycop of the second nitration step, we investigated separately the reaction of 2-nitrotoluene under the conditions described,[2] the same reaction but with dichloromethane in place of tetrachloromethane, and finally with dichloromethane without claycop or acetic anhydride but with the same stoichiometric concentration of nitric acid. Observed first-order rate constants, yields and product ratios are given in Table 1.

It is clear from the results that the use of dichloromethane rather than tetrachloromethane makes no difference and that the presence of claycop and acetic anhydride does not affect significantly the product ratio and does not enhance the rate constant (indeed the reaction is nearly 4 times faster in their absence than in their presence).

These reactions were compared with those in which toluene, rather than 2-nitrotoluene, was the starting material under otherwise identical conditions. Using the results of Table 1 to deduce the fate of 2-nitrotoluene, the initial partitioning of the toluene could be deduced from the observed yields of 2,4-DNT and 2,6-DNT. Results are given in Table 2. These confirm[3] that with claycop and acetic anhydride in tetrachloromethane the *para*:*ortho* nitration ratio in the mononitration is somewhat higher than normal. It is in this step that the higher than normal 2,4-DNT:2,6-DNT ratio in the overall dinitration is generated (though in our hands this ratio was 5.9, not 6.6).

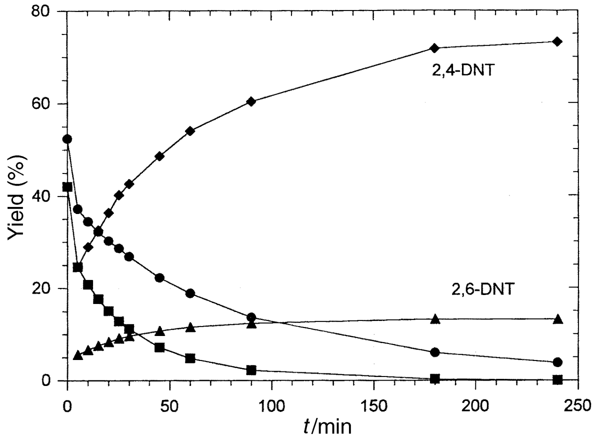

Fig. 1 Yields as percentages of starting aromatic in the nitration of toluene in tetrachloromethane containing claycop, acetic anhydride and nitric acid; (■) 2-nitrotoluene, (●) 4-nitrotoluene, (◆) 2,4-DNT, (▲) 2,6-DNT

Table 1 Yields expressed as percentages of initial aromatic in the reaction of 2-nitrotoluene with nitric acid (stoichiometric concentration 4.2 mol dm^{-3}) at 25 °C

Conditions	Yield	2,4-DNT: 2,6-DNT	$k_{obs}/10^{-4}$ s^{-1}
CCl_4, claycop, acetic anhydride	96%	2.1	7.7
CH_2Cl_2, claycop, acetic anhydride	98%	2.1	8.4
CH_2Cl_2 (no claycop or acetic anhydride)	98%	2.2	30

The high *para*:*ortho* ratio in the first nitration step was not observed using dichloromethane with or without claycop and acetic anhydride, nor was it reported for the homogeneous reaction with 0.3 mol dm^{-3} nitric acid in tetrachloromethane[4] (see Table 2). The reactions of toluene in tetrachloromethane with claycop and acetic anhydride, but in the absence of added nitric acid, were also investigated. They were not first-order, but showed a marked induction period (Fig. 2) followed by more rapid nitration which stopped at the mononitration stage. The reaction gave an *ortho*:*meta*:*para* ratio of 43:5:52, very similar to that deduced for the fast mononitration step under the conditions described in Table 2.

The only source of N^V is the nitrate in the claycop. If all this were made available as nitric acid the concentration of nitric acid in tetrachloromethane would have been 0.48 mol dm^{-3} under which conditions the reaction with toluene (which is zeroth-order in toluene and fifth-order in nitric acid[4]) would

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Table 2 Yields expressed as percentages of initial aromatic in the reaction of toluene with nitric acid (stoichiometric concentration 4.2 mol dm^{-3} unless otherwise stated) at 25 °C

Conditions	2,4-DNT[a]	2,6-DNT[a]	*o*[b]	*m*[b]	*p*[b]	Other[b,c]
CCl_4, claycop, acetic anhydride[d]	77	13	43	4	49	4
CCl_4 (no claycop or acetic anhydride)[e]	—	—	53	3	44	—
CH_2Cl_2, claycop, acetic anhydride	76	16	51	4	43	2
CH_2Cl_2 (no claycop or acetic anhydride)	74	15	50	4	40	6

[a] Final yields after 4 h. The small amount of 4-nitrotoluene remaining at this time has been aggregated with the 2,4-DNT. [b] Initial partitioning in the mononitration step, deduced as described. [c] Undetermined products, possibly resulting from *ipso* attack. [d] Typical procedure: to claycop (2.4 g) in a two-necked flask held at 25 °C, was added tetrachloromethane (10 cm^3), acetic anhydride (7.5 cm^3) and a solution of toluene (0.46 g) and 3,5-dichloronitrobenzene (GC reference standard, 0.40 g) in tetrachloromethane (5 cm^3). The mixture was stirred and 100% nitric acid (7.4 g) was added slowly. Samples were taken at time intervals, quenched in aqueous $NaHCO_3$, extracted and analysed by GC. [e] Nitric acid concentration 0.30 mol dm^{-3}, mononitration only. Results from ref. 4.

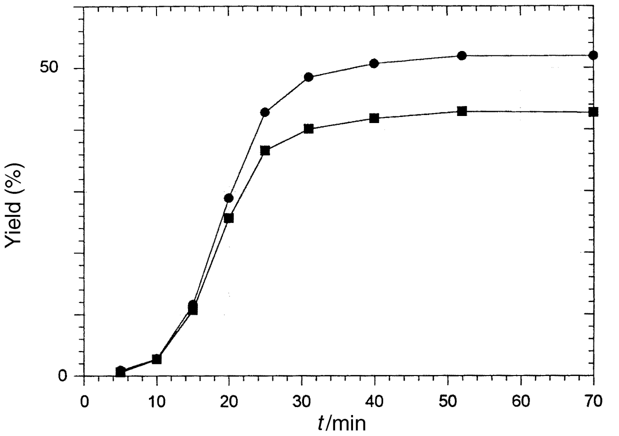

Fig. 2 Yields as percentages of starting aromatic in the nitration of toluene in tetrachloromethane containing claycop and acetic anhydride, but no nitric acid; (■) 2-nitrotoluene, (●) 4-nitrotoluene

have taken 3 h to reach completion.[4] In fact the reaction was complete in 50 min, so it is clear that the claycop has a rate-enhancing as well as a regioselective effect under these conditions.

Conclusions

The presence of claycop and acetic anhydride does not significantly alter the isomer distribution in the nitration of 2-nitrotoluene in dichloromethane or tetrachloromethane containing nitric acid. The rate constant for this kinetically first-order reaction is similar in either solvent. Using dichloromethane, the reaction proceeds more quickly if the claycop and acetic anhydride are omitted. The product distribution, 2,4-DNT : 2,6-DNT, and the relative rates of reaction of 2-nitrotoluene and 4-nitrotoluene are very similar to those found in normal nitronium ion reactions in acid solution.[5]

If toluene is dinitrated under similar conditions the 2,4-DNT : 2,6-DNT ratio is 5.9 with tetrachloromethane, but 4.8 with dichloromethane. The difference arises in the first mononitration step, which shows a higher than normal *para* : *ortho* ratio if the solvent is tetrachloromethane and claycop and acetic anhydride are present.

The reaction in tetrachloromethane with claycop and acetic anhydride in the absence of nitric acid is faster than would be observed in a homogeneous solution containing nitric acid equivalent to the nitrate in the claycop.

Thus claycop and acetic anhydride in tetrachloromethane are modestly catalytic and regioselective in the mononitration of toluene. Claycop and acetic anhydride are neither catalytic nor regioselective in the nitration of 2-nitrotoluene.

Acknowledgements

We thank Dr R. W. Millar and Dr R. P. Claridge for helpful discussions. This work has been carried out with the support of the Defence Research Agency.

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Paper 7/01226H
Received 21*st February* 1997
Accepted 13*th March* 1997