

COMPETITIVE DEUTERATION OF TOLUENE AND TOLUENE- α,α,α -d₃

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INTRODUCTION

The relative rates of deuteration in trifluoroacetic acid of toluene and toluene- α,α,α -d₃ were determined several years ago¹. A difference of approximately five per cent was found; toluene- α,α,α -d₃ deuterating more slowly than toluene. Earlier, it had been shown that the relative rates of deuteration in trifluoroacetic acid of various alkyl benzenes was subject to a solvent effect. When toluene and other monoalkyl benzenes were deuterated at 70°, using 24.6 mole per cent aromatic hydrocarbon, the relative rates of toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, s-butylbenzene and n-butylbenzene were 1 : 0.82 : 0.67 : 0.72 : 0.55 : 0.59. However, when these compounds were deuterated "competitively" with toluene, by comparing the initial rates of deuteration in a solution containing the same concentration of total aromatic, but made up of an equimolar mixture of toluene and the other hydrocarbon being studied, the relative rates were found to be 1 : 1.04 : 0.98 : 1.09 : 0.95 : 1.12. These relative rates were independent of the ratios of the two aromatic components over a 22-fold change in relative amounts provided the total aromatic concentration is not changed. It was therefore considered advisable to re-determine the relative rates of deuteration of toluene and toluene- α,α,α -d₃ using a competitive procedure. This study made use of a mass spectrometric analysis of the deuteration product of a mixture of approximately equal amounts of toluene and toluene- α,α,α -d₃.

EXPERIMENTAL STUDY

Toluene, toluene- α,α,α -d₃ and mixtures of approximately equal amounts of these aromatic hydrocarbons were subjected to mass spectrometric analysis, using low ionizing voltages†. Corrections were made for sample decay. The toluene which was used showed a mass 93/92 ratio of 0.0789. Mass 93 (the $M + 1$ peak) represents the presence of the ¹³C isotope. Its abundance is slightly higher than expected but still well within the range of the natural abundance of ¹³C. In order to estimate the amount of toluene- α,α -d₂ (mass 94) in the sample of toluene- α,α,α -d₃ (mass 95) used in this study the mass 94/95 ratio was examined. This examination was conducted using low ionizing voltages. These voltages were gradually increased with the

† Consolidated Engineering Corp., Model 21-401.

following result: the 94/95 ratio remained constant until fragmentation occurred, after which the 94/95 ratio showed a linear increase. The flat portion of the curve yielded the following 94/95 ratios: 0.0135; 0.0149; 0.0132; 0.0138. These values indicate the presence of approximately 1.4 per cent of toluene- α,α -d₂ in the toluene- α,α,α -d₃ used in this study. An examination of two mixtures of approximately equal amounts of toluene and toluene- α,α,α -d₃ again using sufficiently low ionizing voltages to avoid fragmentation yielded a 93/92 mass ratio of 0.0815. The difference between 0.0815 and 0.0789 (the 93/92 ratio for toluene) is therefore due to the presence of a small amount (0.26 per cent) toluene- α -d₁. The 96/95 ratio found in the case of the undeuterated mixtures was 0.0788 \pm 0.0007.

Two mixtures were subjected to deuteration at 70°; one for three hours and the second for a five-hour period. The deuterating mixture was prepared by diluting five ml of deuterium oxide to one hundred ml with trifluoroacetic acid. The results are shown in *Table 1*.

Table 1. Mass spectrometric analysis

Mass	Three-hour deuteration			Five-hour deuteration		
	(%)	Average	(%)	Average		
92	44.34	44.37	44.36	44.75	44.33	44.54
93	5.01	4.99	5.00	6.12	6.12	6.12
94	0.85	0.85	0.85	0.91	1.02	0.96
95	44.61	44.63	44.62	42.20	42.47	42.34
96	4.91	4.89	4.90	5.68	5.71	5.70
97	0.27	0.27	0.27	0.36	0.36	0.36

DISCUSSION

The data indicate that approximately three and five per cent of the toluene and toluene- α,α,α -d₃ were deuterated in the three-hour and five-hour deuteration conducted in this study. Accordingly, the possibility of the introduction of two deuterium atoms into a single aromatic nucleus was disregarded. *Table 2* shows the percentages of the various reaction products present after the three-hour deuteration.

The values in parentheses are calculated using the experimental value 0.0789 for the $(M + 1)/M$ ratio; and the value 30 for the $(M + 1)/(M + 2)$ ratio. Furthermore, the assumption was made that the rates of deuteration of toluene- α -d₁ and toluene- α,α -d₂ were the same as the rate of deuteration of toluene. Since the amounts of these two side-chain deuterated toluenes were quite small, no appreciable error is introduced by this assumption. On this basis, at the end of the three-hour deuteration the ratio of mono-deuterotoluene (1.38) to toluene (44.36) is 0.0311 and the ratio of mono-deuterotoluene- α,α,α -d₃ (1.38) to toluene- α,α,α -d₃ (44.56) is 0.0310.

In the case of the five-hour deuteration, the significant ratio of mono-deuterotoluene (2.49) to toluene (44.54) is 0.0559 and the ratio of mono-deuterotoluene- α,α,α -d₃ (2.37) to toluene- α,α,α -d₃ (42.26) is 0.0560.

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Mass	Total found				
92	44.36				
93					5.00
	(3.50)	(0.12)	(1.38)		
94					0.85
	(0.11)	(0.22)	(0.01)	D	(0.51)
95					44.62
	** D	* D	*	D	(44.56)
96					4.90
	O	O	O	*	(1.38)
97					0.27
	CD3	CD3			
	(0.12)	(0.22)			

* indicates ¹³C

Table 2. Three-hour deuteration

(Table 2.) Thus, there is no detectable difference between the rates of deuteration between toluene and toluene- α,α,α -d₃ under the conditions used in the experiments here described.

These results are not surprising in view of the results dealing with aromatic substitution reported^{2, 3} previously from different laboratories using widely differing procedures.

The work which was reported⁴ to show a small difference in rates of deuteration in trifluoroacetic acid, can perhaps be reconciled with the present findings in the following manner. In the earlier study the deuterated products of toluene and toluene- α,α,α -d₃ were subjected to an alkaline permanganate oxidation to produce deuterium-containing benzoic acid. It has been established that nuclear-deuterated toluene samples were oxidized under these conditions without loss of deuterium within the limits of the experimental error. However, it is possible that, in the case of

the nuclear-deuterated toluene- α, α, α -d₃ samples, a small amount of deuterium-hydrogen exchange had occurred, since in this case the primary isotope effect operates to lengthen the period required for this oxidation and, therefore, would afford greater opportunity for loss of deuterium in the conversion to benzoic acid.

Mass.						Total found	
92		44.54				44.54	
93		(3.51)	(0.12)	(2.49)		6.12	
94		(0.11)	(0.22)	(0.01)	CH2D D 0 (0.62)	0.96	
95		**D 0	* D 0	CHD ₂ (0.05)	CHD ₂ D (0.03)	CD ₃ (42.26)	42.34
96		** D 0	* D 0	CHD ₂ 0	CD ₃ (3.33)	CD ₃ D (2.37)	5.70
97		(0.11)	(0.37)				0.35

Table 3. Five-hour deuteration

It is instructive to compare the rates of deuteration in trifluoroacetic acid of toluene and t-butylbenzene. Unpublished studies have shown that the difference in the over-all rates in these two cases is not large. The partial rate factors for toluene are o_f 250, m_f 4, p_f 420.

Mackor, Smit and van der Waals have reported⁵ that both rate constants and activation energies for hydrogen-deuterium exchange at the *p*-positions in toluene, ethylbenzene and t-butylbenzene are equal within experimental error. However, the *meta* partial rate factor for t-butylbenzene is approximately three times that of toluene. The contribution of the *meta* partial rate factor is small by comparison with that of the *ortho* and *para* partial factors, so that changes in the rates of deuteration in the *meta* position show

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little influence on the total rates. Since such gross changes as replacement of methyl by the t-butyl group effect only relatively small changes in the total rate of deuteration in trifluoroacetic acid, one would scarcely expect to find any appreciable difference between the total rates of deuteration of toluene and toluene- α,α,α -d₃. Differences in the substituent effects of the methyl and t-butyl groups bring about a three-fold increase in *meta* partial rate factor. Halevi and his co-workers have presented⁶ convincing reasons for assigning small but genuine differences between methyl and deuterated methyl groups by virtue of differences in the ease of inductive or hyperconjugative electron release. The present study has failed to reveal any difference in the rates of deuteration of toluene and toluene- α,α,α -d₃ and it is possible that our method of study was not sufficiently sensitive to detect such a small difference.

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