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AROMATIC SUBSTITUTION BY FREE BENZYL CATIONS FROM THE NUCLEAR DECAY OF MULTI-TRITIATED TOLUENE. COMPETITIVE BENZYLATION OF BENZENE AND TOLUENE IN THE GAS PHASE AND IN SOLUTION

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ABSTRACT

Benzyl cations, free of counter ions, have been generated from the nuclear decay of tritium atoms contained exclusively in the side-chain of multi-labelled toluene and allowed to react in competition experiments with benzene and toluene. The aromatic substitution was studied in both the gaseous and liquid phase, employing pure aromatics or aromatics dissolved in n-hexane, carbon tetrachloride and nitromethane as the reaction medium. In the gaseous systems, at 20 Torr total pressure, high *meta* substitution of toluene indicates extensive isomerization of the excited intermediates, while the increase of the k_T/k_B value in the presence of NH_3 suggests that selective transalkylation competes with proton transfer to ammonia from the benzyl cation adducts with benzene, but not with toluene. High positional and low substrate selectivities were measured in solution, the decrease in k_T/k_B (from 2·8 to 1·7) in the different solvents being accompanied by an increase in the $o/2p$ ratio. Competition experiments between benzene and methanol indicate that the reaction is not diffusion controlled. The influence of the reaction medium on the substrate selectivity is explained by postulating the formation of a cation–solvent adduct, where the solvent molecule undergoes displacement by the substrate. Positional selectivity would be controlled in a subsequent step.

INTRODUCTION

Friedel–Crafts benzylation has been the subject of much work of a synthetic and mechanistic nature.[1] The kinetic results obtained in recent years appeared crucial to the debate regarding the mechanism of electrophilic aromatic substitution.[2–7] The reaction does not generally fit

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Brown's relationship,† displaying a low reactivity ratio (k_T/k_B) in both competitive and non-competitive experiments,[8] which contrasts with the high positional selectivity deduced from the isomeric composition of products from toluene. Further, the substrate but not the positional selectivity appears to be very sensitive to the experimental conditions, e.g. the nature of the benzylating reagent, the catalyst and the purity of the solvent.[3,6,7]

To explain these and other results, Olah[4] postulated a variable transition-state mechanism for electrophilic aromatic substitution, where the substrate selectivity of strong electrophiles, such as the benzyl cation, is determined by an early transition state leading to the formation of an oriented π-complex, which in turn evolves into isomeric Wheland intermediates, substituted at *ortho*, *meta* and *para* positions.

DeHaan *et al.*[6c] noted that the formation of benzylating electrophiles by Friedel–Crafts catalysts is rate determining, except for *p*-nitrobenzylation, the attack on the aromatics of the reacting species, i.e. benzyl cations or possibly a cation–catalyst anion pair, taking place in a fast step. Therefore, following Jencks' approach,[9] they suggested as an alternative explanation for the low substrate selectivity the possibility that this reaction step occurs at or near to the diffusion-rate limit. This would not conflict with the observed high positional selectivity, according to an argument given by Rys.[6c,10]

Since a clear characterization of the attacking electrophile is undoubtedly necessary for the understanding of the reaction mechanism, we decided to investigate the benzylation of aromatics by originally free benzyl cations, produced by the nuclear decay of tritium atoms contained in the methyl group of specially prepared multi-labelled toluene.

The technique, developed many years ago in our laboratories[11] and already applied to the electrophilic tritiation and methylation of aromatics,[12,13] allows one to generate within any homogeneous system of interest randomly distributed carbenium ions of well defined structure and initial charge location, lacking a counter ion, their positive charge being balanced by a far removed electron. The nuclear process responsible for their formation is independent of the medium employed, and the presence of residual radioactive labels makes it easy to follow their reactions through the analysis of the neutral end products. These unique features make the experimental approach eminently suited to the study of competitive reactions, in the absence of complicating and undesirable effects such as phase separations and changes in the kinetic law of formation of the reagent caused by the moisture inevitably present in the system, or mixing problems which often affect Lewis acid catalysed alkylations.[7]

This present paper describes the results obtained in study of the competitive reaction of nucleogenic benzyl cations with benzene and toluene under widely different conditions, including experiments in the gas phase, in excess liquid aromatics and in n-hexane, carbon tetrachloride and nitromethane solutions of the aromatic substrates.

EXPERIMENTAL

All the reagents and solvents employed for the preparation of the decay systems, the inactive carriers or the standards for gas–liquid chromatographic (GLC) or high-performance liquid chromatographic (HPLC) analyses were commercially available samples, unless stated otherwise.

Authentic samples of the isomeric benzyltoluenes were prepared according to established procedures[3a] from the reaction of the corresponding xylyl chlorides with benzene in the

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† An exception is provided, for example, in Reference 7 by the $TiCl_4$-catalysed reaction of benzyl chloride in excess aromatics.

presence of $AlCl_3$–CH_3NO_2, and purified by preparative GLC on the same columns as used for the analysis of products.

Labelled toluene, containing at least two tritium atoms exclusively in the side-chain, was prepared, diluted with inactive toluene to a specific activity of 25·4 Ci mol^{-1}, purified and isotopically checked by the method of Cacace *et al.*[14]

The gaseous samples were prepared by introducing tracer amounts of radioactive $C_6H_5CX_3$ (0·6 mCi) and appropriate amounts of the substrates, contained in fragile glass ampoules, into carefully outgassed and evacuated 500-ml Pyrex bulbs. After addition of the gaseous components (oxygen, employed as a radical scavenger, and ammonia, when required) by conventional techniques in a greaseless vacuum line, the bulbs were cooled at −196 °C and sealed off. The ampoules were then broken and the components allowed to mix at room temperature.

The liquid samples, prepared by dissolving tracer amounts of the labelled precursor (0·6 mCi) in 2 ml of the substrate solution, were introduced into Pyrex vials equipped with a capillary neck sealed by a mobile mercury plug, which ensures complete filling of the volume by the liquid phase.

All the samples were stored in the dark at 25 °C. After the decay time (12 months), the vessels were cooled, opened, carefully washed with methanol in the case of gas-phase systems, known aliquots of inactive carriers were added and the contents analysed by radio-GLC and HPLC, after thorough mixing.

A Carlo-Erba Model C gas chromatograph equipped with a hot-wire detector and connected to a Berthold 80-ml internal flow proportional counter, heated at 160 °C, was employed for the analyses. Helium was used as the carrier gas at a flow-rate of 24 ml min^{-1} for the following columns: (i) 5-m SP-1200 (5%)–Bentone 34 (1·75%) on Supelcoport (80–100 mesh), operated at 160 °C; (ii) 4-m SP-1000 (10%) on Supelcoport (100–120 mesh), operated at 200 °C. A helium–methane (1 : 3) gas mixture (25 ml min^{-1}) was added to the effluents to obtain an appropriate blend for proportional counting.

HPLC analyses were carried out on a Perkin-Elmer Series-3B chromatograph equipped with a 15-cm Rofil C-18 (5 μm) column from Alltech, eluted with water–methanol (40 : 60) at a flow-rate of 1 ml min^{-1}, and connected to a UV detector set at 300 nm, in series with a Berthold LB 503 HS flow liquid scintillation counter.

The identity of the tritiated products was established by comparison of their retention volumes with those of authentic samples, and their yields were determined by comparison of the measured activities with the area of the corresponding inactive carrier elution peaks.

RESULTS

The results of competitive experiments, carried out with equimolar amounts of benzene and toluene, are reported in Table 1. Each substrate was introduced at a 10 Torr partial pressure in the gaseous systems together with O_2 and NH_3, when necessary, or at a 0·3 M concentration in the solvents employed. Competitions in a mixture of the pure liquid aromatics and between benzene and methanol in n-hexane were also carried out, with the aim of estimating the order of magnitude of the absolute rate constants of the reaction of benzyl cations with the substrates. In fact, the absolute rate constant of the reaction with methanol has been measured in pulse radiolysis experiments.[15]

The total radiochemical yields of products are expressed as the ratio of their activity to that of the labelled benzyl cations produced during the storage period, calculated from the initial activity of $C_6H_5CX_3$, the half-life of tritium, and decay time and the average number of tritium

Table 1. Competitive reaction of decay-produced benzyl cation with benzene and toluene

System composition		Yield of product (%)			Isomeric composition benzyltoluene (%)		
	Substrates	Total	$PhCH_2X$	Apparent relative reactivity[a]	*o*-	*m*-	*p*-
Gas	C_6H_6, 10 Torr C_7H_8, 10 Torr	68·8		3·0	10	64	26
Gas	C_6H_6, 10 Torr C_7H_8, 10 Torr NH_3, 10 Torr	47·6		5·8	23	51	26
Liquid	$C_6H_6 + C_7H_8$	64·5	5·1 (X = OH)	2·8	47	5	48
n-C_6H_{14}	C_6H_6, 0·3 M C_7H_8, 0·3 M	81·2	6·4 (X = OH)	1·9	54	19	27
CCl_4	C_6H_6, 0·3 M C_7H_8, 0·3 M	81·4	23·8 (X = Cl)	1·7	60	6	34
CH_3NO_2	C_6H_6, 0·3 M C_7H_8, 0·3 M	62·6	19·5 (X = OH)	2·7	56	$\leqslant 0·1$	44
n-C_6H_{14}	MeOH, 0·6 M C_6H_6, 0·6 M	75·0		1·2[b]			

[a] Calculated with respect to benzene by assuming first-order dependence on the substrates concentration; s.d. = 10% (see text).

[b] Corrected to account for methanol dimer formation.

atoms per molecule, measured from the yield of diphenylmethanes in independent experiments involving the decay of $C_6H_5CH_3$ in a large excess of liquid benzene-d_6.[14]

Significantly, the expected diphenylmethane and isomeric benzyltoluenes are the major aromatic neutral end-products from all experiments; in the pure aromatics and in n-hexane solution minor yields of benzyl alcohol were also recovered, possibly owing to reaction of the benzyl cations with residual moisture present in the system or on the walls. Higher yields of the alcohol in nitromethane and the isolation of benzyl chloride in tetrachloromethane are indicative of possible reactions of initially excited ions with the solvent.

The reported k_T/k_B ratios were calculated by assuming a first-order dependence of the rates of the substrate concentration. All the analyses were carried out at least in triplicate, and the results are affected by a standard deviation of $\leqslant 10\%$.

DISCUSSION

Formation of the reagent

As a consequence of the β^- decay, a tritium atom changes into ^3He and a positive charge is generated into the precursor molecule within a time ($\leqslant 10^{-15}$ s) that is very short on the chemical reactivity scale, and therefore the process is largely independent of the medium employed. The C—He bond undergoes rapid fission, owing to the repulsive nature of its potential energy curve,[16] and, in the case of benzyl tritide, a free benzyl cation is produced in the system:

$$C_6H_5CX_3 \rightarrow [C_7H_5X_2{}^3He]^+ \rightarrow {}^3He + C_6H_5CX_2^+ \tag{1}$$

The results of both charge mass spectrometry[17] and theoretical treatments[18] show that daughter ions in their ground electronic state are generated from ca 80% of the decay events, the remaining 20% being formed in highly excited states prone to extensive fragmentation into reactive species whose possible products do not interfere with those of interest to this work.

As a conclusion, benzyl cations of well characterized structure are formed from multi-labelled toluene, in the absence of counter ions and with a random spatial distribution within the system. Since the activity levels employed are extremely low, any self-radiolytic effect can safely be neglected, and the presence of a second tritium atom in the cation allows the detection of very small traces of products by sensitive radiochemical methods.

The reagent is formed by a rapid process with a geometry reminiscent of that of the parent molecule; this means that the benzyl cation originally has a pyramidal structure whose upper excitation energy limit with respect to the most stable planar structure can be estimated as ca 30 kcal mol^{-1}, in comparison with the correspondingly deformed methyl cation.[19] This is not a problem in solution, where the high collision rate with the medium allows efficient relaxation of the reagent; it should be considered, instead, in the low-pressure gas-phase experiments, where only intramolecular relaxation can occur prior to interaction with the substrate.

Nevertheless, previous experiments in gaseous methanol[20] at high pressure showed that the decay produced benzyl cations do not undergo isomerization reactions during the time (10^{-9}–10^{-7} s) required for their trapping, and therefore retain their original structure, even in the gas phase.

Gas-phase benzylation

The stability and reactivity of the benzyl cation with respect to its isomers has been extensively studied by mass spectrometric methods in the low-pressure range, from 10^{-5} Torr in ICR experiments[21] to a few Torr in 'high-pressure' MS.[22,23] Addition to toluene [equation (2)] gives ions **I** of $m/z = 183$ which, depending on the pressure and temperature, may dissociate back to the reagents or to an ion of $m/z = 105$ [equation (3)], corresponding to the xylyl cation. This is the product detected under ICR conditions, where the adduct ions cannot be observed even at room temperature, owing to exceedingly inefficient collisional stabilization.

$$C_6H_5CH_2^+ + C_6H_5CH_3 \rightarrow \underset{\textbf{I}}{C_6H_5CH_2C_6H_5CH_3^+} \qquad (2)$$

$$\textbf{I} \rightarrow C_6H_6 + CH_3C_6H_4CH_2^+ \qquad (3)$$

The γ-radiolysis of toluene, ethylbenzene and *m*-xylene at a few Torr total pressure led to formation of the corresponding alkylated diphenylmethanes as the major products.[24]

The absence of radioactive xylylated products from the decay experiments show either that reaction (3) does not take place above 20 Torr, although the benzyl cations might originally possess excess vibrational energy, or, less likely, that xylyl ions are unreactive towards toluene.

The addition of benzyl ions to benzene and toluene is expected to the exothermic by ca 13·4 and 21·9 kcal mol^{-1}, respectively, based on a proton affinity value of the ring position bearing the benzyl substituent equal to that of an unsubstituted position (proton affinity values taken from Ref. 25a and $\Delta H_f°$ of neutral species from Reference 25b). The estimated $\Delta H°$ for the reaction with NH_3 is ca $-34·8$ kcal mol^{-1} ($\Delta H_f°$ of benzylamine from group additivity from Reference 26).

Although the amount of benzylamine formed could not be measured reliably, owing to exchange and counting problems, the decrease in the total yield in the presence of ammonia roughly accounts, as expected from the relative concentration of nucleophiles in the system, for one third of the benzyl ions produced.

The apparent increase in substrate selectivity in the presence of NH_3 indicates an appreciable discrimination in an exothermic gas-phase alkylation. On the other hand, the isomeric composition of the products from toluene shows exceedingly high yields of *meta* substitution, which decrease in favour of *ortho* in the presence of a base, suggesting that *ortho*-substituted arenium ions can rearrange into the *meta* isomers.

Certainly, the experimental conditions employed, i.e. the relatively low pressure and the absence of a collision gas, do not favour efficient transfer of the excess energy originally present in the benzyl cations from their formation process or imparted to the intermediates by the exothermicity of the reaction. Therefore, fast isomerization towards a thermodynamically controlled distribution of products may take place, unless the gaseous Wheland intermediates are efficiently quenched by collisions and/or rapidly deprotonated by a base, as is the case of other gas-phase alkylations.[13,27] Moreover, back-dissociation of the excited adducts to the reagents could occur in this system and also affect, in favour of toluene, the substrate selectivity; evidence against this possibility is provided, however, by the observed increase in the reactivity ratio in the presence of ammonia, which should reduce the effect by intercepting the benzyl cations and shift the selectivity in the opposite direction. The results rather suggest that selective transalkylation from the adducts of benzene, but not of toluene, to ammonia competes to some extent with deprotonation.

In this view, the reported reactivity ratio should be considered simply as indicative, representing only an upper limit of the true substrate selectivity. Further studies on the gas-phase benzylation by other techniques are in progress in the laboratory to clarify the point.

Benzylation in solution

The situation is different in the liquid phase, where efficient relaxation of the reagent and of the intermediates with the medium can take place. Here high positional and relatively low substrate selectivity are observed, as generally noticed in traditional Friedel–Crafts benzylation. However, significant system-to-system variations were found in the apparent relative reactivity of benzene and toluene.

In the first place, the rate of the overall alkylation process is limited, under the conditions employed, by the rate of formation of the benzyl cations from the decay of the labelled precursor, which can be calculated from the decay constant of tritium, the average number of tritium atoms in labelled toluene and its concentration in the system, to be ca 2×10^{-14} mol l^{-1} s^{-1}. The electrophile is therefore generated at extremely low concentrations from a uniformly distributed precursor, subject to statistical nuclear events absolutely independent of the medium employed, and may select between the competing substrates.

If any appreciable contribution by vibrationally excited benzyl cations were to be expected in the liquid phase, it would tend to level the substrate selectivity and its effect would be most evident in the neat aromatics. The observation, instead, just in this system of the highest k_T/k_B ratio suggests that the electrophile must undergo a number of unreactive collisions with the medium sufficient to dissipate its excess energy before reacting with a substrate molecule. Therefore, the present results are likely to concern the reactivity of a bona fide free benzyl cation in thermal equilibrium with the medium.

Since the reported results do not fit Brown's selectivity relationship, one might expect, as already suggested,[6c] that the free benzyl cations could react with the substrate faster than they can diffuse and therefore display disguised selectivity. Competition experiments between methanol and benzene were carried out to test this possibility.

The benzyl cation reacts with methanol in 1,2-dichloroethane with a rate constant $k_m = 6 \times 10^7\,\text{mol}^{-1}\,\text{l}\,\text{s}^{-1}$ for the monomer and $K_e k_d = 2 \times 10^8\,\text{mol}^{-2}\,\text{l}^2\,\text{s}^{-1}$ for the dimer, where K_e represents the equilibrium constant for dimerization, several orders of magnitude lower than the diffusion-controlled limiting values.[15]

At the CH_3OH concentration employed in our experiments, i.e. 0·6 M, appreciable amounts of the dimer are likely to be present. From infrared spectroscopic measurements in CCl_4,[28] $\Delta H^\circ = -9{\cdot}2\,\text{kcal mol}^{-1}$ and $\Delta S^\circ = -28$ e.u. at 298 K, leading to an estimate of $K_e \approx 4$ for the dimerization reaction. Assuming hydrogen-bond formation to be not much influenced by differences in the solvents, both CH_3OH and $(CH_3OH)_2$ appear to react at nearly the same specific rate.

Allowing for dimer formation in our experiments, $k_{MeOH}/k_B = 1{\cdot}2$, leading to an estimate of the absolute rate constant value for the benzylation of benzene of the order of $5 \times 10^7\,\text{mol}^{-1}\,\text{l}\,\text{s}^{-1}$; this makes any correction for non-equilibrium distribution of reactant concentration negligible in our systems when compared with diffusion-controlled limiting value of $2 \times 10^{10}\,\text{mol}^{-1}\,\text{l}\,\text{s}^{-1}$, estimated by the Smoluchowski equation ($k_{obs} = 4\pi r D'$),[29] assuming reasonable estimates for the separation of the centres of the reacting molecules $r = 5$ Å and the coefficient of mutual diffusion $D' = 5 \times 10^5\,\text{cm}^2\,\text{s}^{-1}$.[30]

It therefore appears very likely that the reaction of benzyl cations with benzene and toluene is not diffusion controlled under the experimental conditions employed, as also indirectly suggested by the observation that the much more reactive decay-produced methyl cation does not dramatically deviate from the reactivity–selectivity relationship ($k_T/k_B = 2{\cdot}3$; 40·1% *o*-, 27·0% *m*-, 32·9% *p*- in the pure aromatics at different concentration ratios).[13]

Our results show an influence of the medium on the substrate and the positional selectivity of the reagent; the data also indicate that a decrease in the k_T/k_B ratio is also accompanied by an increase in the $o/2p$ ratio, in accordance with Olah *et al.*'s suggestion of an 'early' transition state reflecting the charge distribution of the starting aromatics.[3c]

Certainly, the least solvated attacking reagent is to be sought in n-hexane, where, incidentally, the lowest deviation from Brown's relationship was found ($b = \log f_p/S_f = 1{\cdot}1$). However, the high yield of *meta* substitution (19%) also shows that the Wheland intermediates survive long enough in this solvent to undergo extensive isomerization.

As shown by spectroscopic measurements, aromatic hydrocarbons form weak complexes with tetrachloromethane, where the aromatic molecule represents the electron donor to the halogen atom.[31] This helps to explain the low substrate selectivity in CCl_4, since the nucleophilic character of toluene should be comparatively depressed with respect to benzene by such an interaction with the solvent. On the other hand, the isomeric distribution of benzyltoluenes appears kinetically controlled and displays an $o/2p$ ratio of 0·9.

The substrate selectivity measured in the pure benzene–toluene system is set among the lowest levels observed in Friedel–Crafts benzylations in excess aromatics,[3c,7] and the positional selectivity displays lower *para* substitution in favour of *ortho* substitution. This can be understood since the original electrophile in our case is the free cation and not a cation–catalyst anion pair.

In nitromethane, the k_T/k_B ratio is comparable to that obtained in the presence of Lewis acids[3,6,7] and the isomeric distribution of products differs for higher *ortho* substitution and the virtual absence of *meta* substitution. Moreover, in the latter system, isolation of appreciable amounts of benzyl alcohol, which cannot be traced back to reaction with water contained in

CH_3NO_2, accounting for ca one third of the total products yield, indicates a strong interaction of the originally free cation with the polar solvent.

It is therefore suggested that the relatively higher substrate selectivity in CH_3NO_2 can be best understood by assuming formation of an electrophile–solvent adduct where the 'solvent' is displaced from by a substrate molecule.

The low reactivity of the *meta* position of toluene with respect to a position of the benzene ring, and hence the disagreement with Brown's relationship, together with the proposed substitution mechanism are consistent with a rate-limiting step determining the substrate selectivity.

$$C_6H_5CH_2^+ + \text{Solv.} \rightarrow [C_6H_6CH_2\cdots\text{Solv.}]^+ \xrightarrow[-\text{Solv.}]{+\text{Subs.}} [C_6H_6CH_2{-}\text{Subs.}]^+ \rightarrow \sigma\text{-complexes} \quad (4)$$

In this view the positional selectivity would be controlled at a later stage, involving the formation of the σ-complexes. At this level, the absence of interaction by a counter ion and the enhanced role of the solvent may justify the difference observed in the isomeric distribution of products.

In conclusion, these data concerning an originally free benzyl cation have shown that, apart from any quantitative interpretation which deserves more extensive results, the effect of the reaction medium on reactivity and selectivity towards aromatic substrates is enhanced in the absence of the strong and indiscriminate electrostatic interaction with a counter ion.

The action of the solvent takes place at two levels: (i) it may form an adduct with the electrophile so that the substitution can be looked upon as a displacement of the interacting solvent molecule by the substrate, thus influencing the substrate selectivity, and (ii) it perturbs the charge density in the electrophile–substrate complex, determining the final product distribution.

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