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Communications to the Editor

Aromatic Substitution in the Liquid Phase by Bona Fide Free Methyl Cations. Alkylation of Benzene and Toluene

Sir:

We report the first application, concerning a typical aromatic substitution such as the liquid-phase methylation of benzene and toluene, of a new technique designed to generate *free* carbocations of specified structure in any liquid environment and to investigate their reactivity, using as a source of the charged electrophiles appropriate, tritiated precursors, dissolved at a tracer concentration within the liquid substrate(s).

The decay of a radioactive atom in tritiated methane is known from theoretical[1,2] and mass spectrometric[3] studies to yield thermal methyl cations in over 80% of the nuclear transitions. Tracer amounts of methane-t_4, prepared, purified, and analyzed as described in earlier reports,[4] were dissolved in carefully outgassed toluene or benzene–toluene mixtures at a typical specific activity of 300 μCi mL^{-1}, corresponding to a CT_4 concentration of 2.5×10^{-6} mol L^{-1}, and the samples were stored at 22 °C in the dark for 9 months in Pyrex vessels entirely filled by the liquid and equipped with a capillary neck sealed by a mobile mercury plug. After removal of the undecayed CT_4 and careful washing of the liquid with excess CH_4, the samples were analyzed by radio GLC, using a Hewlett-Packard Model 7620 A instrument equipped with a 12-m Bentone 38 + DC 200 silicone oil glass column operated at 140 °C, monitoring the activity of the effluents with a 10-mL internal flow proportional counter heated at 150 °C. The tritiated products were identified by comparing their retention volumes with those of authentic specimens under identical chromatographic conditions, and their relative yields are given in Table I.

The *absolute* overall yield, defined as the ratio of the combined activity of the products identified to the total activity of the CT_3^+ ions formed within the liquid, calculated from the initial activity and the isotopic composition of the tritiated methane (CT_4, 60.4 ± 0.5%; CHT_3, 29.4%; CH_2T_2, 8.1%; CH_3T, 2.0%), the decay rate of T, the storage time, the abundance of the methyl cations formed from the decay, and the efficiency of the detector, show that the products listed in Table I account for 50 ± 10% of the decay ions' activity, without significant differences among the systems investigated. Furthermore, the total activity of the crude liquid, after removal of the undecayed CT_4, matches almost exactly the combined activity of the products identified by GLC, excluding the presence of other tritiated species in the liquid, and suggests that the activity balance must be provided by some gaseous products, e.g., HT or partially tritiated methanes, removed together with CT_4 when the sample is outgassed.

The following discussion will be restricted to the ring methylation of the arenes, the only channel directly and exclusively related to the reactivity of CT_3^+, neglecting other processes, e.g., tritiodeprotonation of the substrate where contribution of the various charged and neutral decay fragments, formed in ~18% of the β transitions, cannot be a priori ruled out.

The methyl cation that the nuclear transition brings into being in the site formerly occupied by the methane molecule in a time very short on the chemical reactivity scale[5] *is absolutely free* since it is not associated with any counterion, its positive charge being neutralized by an electron far removed in the liquid. Moreover, although one might argue that the only unsolvated carbocations are to be found in the dilute gas state, the decay CT_3^+ ion is undoubtedly as unsolvated as conceivable for a charged species in a condensed phase. In fact, owing to the very high collision frequency with the molecules of the liquid substrate(s) and to the proven ability of the methyl ion to react at a rate approaching collision frequency even with relatively weak nucleophiles,[6] its attack of arenes is likely to

Table I

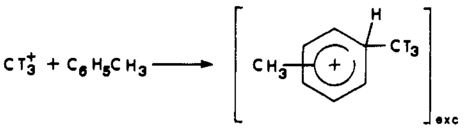
Liquid composition, mole fraction		Relative yields of products,[a] %						
Benzene	Toluene	Unknown[b]	Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
	1.00	2.6		13.9	4.2	32.1	21.4	25.8
	1.00	2.7		13.8	4.5	31.5	21.2	26.3
0.50	0.50	1.5	8.0	36.0	1.5	20.7	14.3	18.0
0.09	0.91	2.1	2.0	18.4	2.8	29.9	20.0	24.8
0.91	0.09	0.5	14.0	69.6	0.2	6.1	4.3	5.5

[a] Percentage of the activity contained in each product referred to the total activity of the products isolated. Each value represents the average of the least two independent measurements. The reproducibility of the data is illustrated by comparison of the first two lines. [b] The elution volume of this product is very close to, if lower than, that of ethylbenzene.

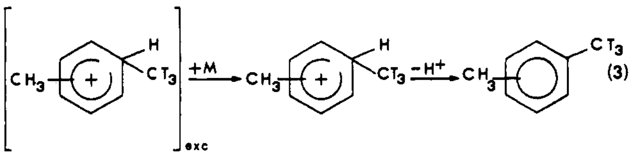
occur in a much shorter time than necessary for the formation of an organized solvation sphere, which requires, inter alia, rotational relaxation of dipolar molecules in the field of the cation.

$$CT_4 \xrightarrow{\text{beta decay}} CT_3^+ + {}^3He + \beta^- \qquad (1)$$

Several exothermic reaction channels are available to the decay methyl cation. Apart from hydride-ion abstraction, energetically allowed from both C_6H_6 and C_7H_8[7] and leading directly to the formation of partially tritiated methanes, alkylation of the arenes is also strongly exothermic, with a $\Delta H°$ value of the order of -100 kcal mol^{-1} for process 2.[8]



The highly excited arenium ions can either fragment, yielding for instance HT, partially tritiated methanes, etc., or be stabilized by the very effective collisional deactivation processes occurring in the liquid. The stabilized arenium ions can eventually lose a proton to any base contained in the system, including the substrate itself, thus giving the observed methylated products (eq 3), whose (relatively close) yields from C_6H_6 and C_7H_8 suggest that the rates of the alkylation and fragmentation processes are comparable for the two substrates.



Concerning the *substrate* selectivity of the reagent, the apparent[9] k_T/k_B ratio, referred exclusively to ring alkylation, i.e., to methyl for hydrogen substitution at the aromatic nucleus, can be approximately estimated from the results of the competition experiments. Interpretation of the data is complicated by the formation of appreciable amounts of tritiated toluene from C_7H_8, as well as from C_6H_6, which helps to explain the considerable scatter of the corrected k_T/k_B ratios obtained from a best fit treatment, i.e., 2.35, 2.19, and 2.39, respectively, for $[C_7H_8]:[C_6H_6]$ ratios of 10.0, 1.00, and 0.10.

The *positional* selectivity of the CT_3^+ attack is reflected by the isomeric composition of the xylenes, 40.1 ± 0.4% ortho, 27.0 ± 0.1% meta, and 32.9 ± 0.6% para from pure toluene, which underlines the electrophilic character of the alkylation and finds close analogies to the behavior of HeT^+, the only other free cation whose reactivity has been investigated in the liquid phase.[10]

To our knowledge, in the search to substantiate the long-postulated[11] role of carbonium ions in Friedel-Crafts alkylation, the present study provides the first data concerning a reagent whose +1 charge state and lack of a counterion are positively established *in the liquid phase.*[12] The approach outlined in the present communication appears of potential mechanistic value in order to evaluate the intrinsic reactivity of the most simple carbocation, unperturbed by the effects of the anion, the catalyst, etc., that have complicated all too frequently the study of aromatic alkylation.[13] Extension of the decay technique to the solid state is also conceivable. More detailed investigations on the electrophilic reactivity of *free* CT_3^+ decay ions, in particular a comparative study of their attack to gaseous and liquid arenes, are in progress and will be reported in due course.

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(8) Value arrived at by taking $\Delta H_f°$ 258 kcal mol^{-1} for CH_3^+ (see J. L. Franklin in "Carbonium Ions", Vol. 1, G. A. Olah and P. v. R. Schleyer Ed., Interscience, New York, N.Y., 1968, p 85) and assuming the PA of the methyl-substituted ring positions of the xylenes correspondent to that of toluene (see R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98,** 1320 (1976).
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The Importance of Leaving Group Steric Effects in Solvolysis of Tertiary Carbinyl Systems

Empirical Force Field Treatment of Acid-Catalyzed Dehydration of 2-Alkyl-2-adamantanols

Sir:

We wish to report that replacement of a methyl group by a *tert*-butyl group in 2-alkyl-2-adamantanols, **1,** increases the dehydration rate by a factor of 1820, whereas the *t*-Bu/Me ratio in the solvolysis of the corresponding *p*-nitrobenzoates, **2,** is 225 000.[1] Empirical force field calculations[2] show that the hydrocarbon-cation model is in good agreement with the dehydration data but leaving group steric effects are to a large extent responsible for the very high *t*-Bu/Me ratios in the solvolysis of strained tertiary carbinyl *p*-nitrobenzoates.

The steric requirements of OH and OPNB have frequently been stated to be similar, at least in norbornyl derivatives.[3] In the alkydi-*tert*-butylcarbinyl system, however, the *t*-Bu/Me ratio goes from 0.08 to 60 when the leaving group is changed from water[4] to OPNB.[5] The alkyldi-*tert*-butylcarbinols are highly congested species and, perhaps, atypical. We undertook therefore to reexamine the effect of replacing OH by OPNB in a more representative system.