

Protonation of Simple Aromatics in Superacids. A Reexamination

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The interest in species resulting from additions of protons or other cations to aromatic rings has existed for a long time.¹ Thus, in 1921, Schneider and Seebach reported that 1,3,5-trianisylbenzene reacted with bromine at dry ice temperature to form a green crystalline material that upon warming lost hydrogen bromide and formed the bromine substitution product.² That was not the first time that adducts of electrophiles with aromatics, crystallizing at low temperature, were observed; complexes of aluminum chloride and aluminum bromide with benzene and toluene had been discovered in 1878.^{3,4} However, the adduct of Schneider and Seebach was the first species identified as the ionic (saltlike) intermediate of an aromatic substitution, by Pfeiffer and Wizinger, in 1928.⁵ Their article offered the mechanism of the electrophilic aromatic substitutions and proposed the intervention as *intermediates* of what are called today σ complexes,⁶ arenonium ions,⁷ or arenium ions.⁸ It also explained the activation/deactivation and ortho-para vs. meta orientation by the preexistent substituents and the role of catalysts.⁹ The paper was ahead of its time and was overlooked by subsequent workers. For instance, in 1939 Norris and co-workers prepared complexes of alkylbenzenes with $\text{AlBr}_3\text{-HBr}$ and $\text{AlCl}_3\text{-HCl}$ ¹⁰ as well as "ionized" adducts $[\text{ArH}\cdot\text{EtBr}\cdot\text{AlBr}_3]$, which they showed to be intermediates of the alkylation reaction.¹¹ Yet, no structure was proposed for these compounds.^{10,11}

In the same period, Hughes and Ingold,¹² and then Wheland,¹³ apparently unaware of the previous work, wrote structures virtually identical with Pfeiffer and Wizinger's,⁵ but they did not consider these as intermediates, but transition states, or rather one of the limiting structures that contribute to the "resonance hybrid" which is the transition state of the aromatic substitution,^{12,13} the other limiting structure having the electrophile "merely close to the carbon atom being attacked, but ... not joined to it by a covalent bond".¹³ Nevertheless, cyclohexadienyl ions have been referred to as Wheland intermediates; there seems to be only one paper, by Olah, in which the more appropriate term of Pfeiffer-Wizinger complexes is used.¹⁴

The direct investigation of protonated aromatics was restarted after 1950,^{6,15-19} when the arenium structure for the cations was secured by the work of Brown^{6,15} and Gold.¹⁷ Spectroscopic methods, like UV,¹⁷⁻¹⁹ IR,²⁰ and NMR,^{7,21} began to be used routinely. After 1960, NMR became the main investigative tool, and the number of papers exploded.¹

Dan Fărcașiu was born and educated in Romania. After arriving in the U.S.A., he carried out postdoctoral research (and some teaching) at City College of New York and Princeton University. Since 1974, he has been working in the Corporate Research-Science Laboratories of Exxon Research and Engineering Co., mostly on physical-organic and synthetic problems related to strong acid chemistry and catalysis.

Our work in this field stemmed from the research initiated at Exxon in the area of nontraditional strong acid catalysts for hydrocarbon conversions.²² We were interested in the effect of aromatics, particularly benzene, upon the isomerization of alkanes and in the mechanism of catalyst deactivation observed in the presence of aromatics. During our studies we discovered that, despite the large number of publications devoted to the protonation of aromatics, some open questions existed even for the simplest members of the class, benzene and alkylbenzenes. From our work on these species, we reached new conclusions concerning (a) the degree of protonation in various superacids, (b) the site of protonation relative to alkyl substituents, (c) the relative strength of directing effects of different alkyl groups on protonation, and (d) the position of the dealkylation/realkylation equilibrium for protonated

(1) The field has been extensively reviewed; see, for instance: (a) Brouwer, D. M.; Mackor, E. L.; MacLean, C. "Carbonium Ions"; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley: New York, 1970; Vol. 2, p 864. (b) Olah, G. A., Ed. "Friedel-Crafts and Related Reactions"; Interscience: New York, 1963-1964; Vol. 1-4. (c) Olah, G. A. "Friedel-Crafts Chemistry"; Wiley: New York, 1973. (d) Koptuyg, V. A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1081. (e) Koptuyg, V. A., Ed. "Sovremennyye Problemy Khimiy Karbonievyykh Ionov"; Izd. Nauka, Sib. Otdel, Novosibirsk, USSR, 1975, especially p 5. (f) For a historical account, see: Nenitzescu, C. D., in ref 1a, Vol. 1, 1968, p 1.

(2) Schneider, W.; Seebach, F. *Ber. Dtsch. Chem. Ges.* 1921, 54, 2301.

(3) Gustavson, C. G. *Ber. Dtsch. Chem. Ges.* 1878, 11, 1841, 2151.

(4) It was later recognized that such complexes contained HCl or HBr as well: (a) See ref 10 and 11. (b) Baddeley, G. J. *Chem. Soc.* 1950, 994.

(5) Pfeiffer, P.; Wizinger, R. *Liebigs Ann. Chem.* 1928, 461, 132.

(6) Brown, H. C.; Brady, J. D. *J. Am. Chem. Soc.* 1952, 74, 3570.

(7) Doering, W. v. E.; Saunders, M.; Boyton, H. G.; Earhart, H. W.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* 1958, 4, 178.

(8) (a) Olah, G. A. *J. Am. Chem. Soc.* 1972, 94, 808. (b) IUPAC Definitive Rules for Nomenclature of Organic Chemistry, Section C, No. 82.4, cited in ref 8a.

(9) (a) Reference 5 also describes the bromination of olefins $\text{R}_2\text{C}=\text{CR}_2'$ as involving the ions $\text{R}_2\text{C}^+-\text{CR}_2'\text{Br}$ (analogues to the protonation products $\text{R}_2\text{C}^+-\text{CHR}_2'$) which can add Br^- or eliminate H^+ . (b) The authors give credits to H. Meerwein (*Z. Angew. Chem.* 1925, 38, 815) for a related, albeit less clear-cut, representation of the aromatic substitutions, and to W. Dilthey (*J. Prakt. Chem.* [2] 1925, 109, 273) for "the theory and formulation of carbonium salts".

(10) (a) Norris, J. F.; Rubinstein, D. *J. Am. Chem. Soc.* 1939, 61, 1163;

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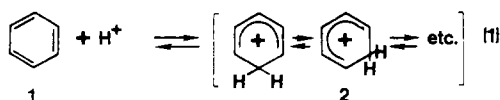
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tertiary alkylbenzenes.²³ These conclusions resulted mainly from the examination of the behavior of each species under consideration in two superacids of significantly different acid strength.

Degree of Protonation of Benzene and Alkylbenzenes in Various Acids. Evaluation of Superacid Strength

The degree of protonation of a given aromatic substrate is obviously determined by the acidity of the medium. Although all are known as superacids,²⁴ the acidic strengths of various systems employed vary widely. Thus, a small amount of mesitylene was evidenced besides its protonated form in HF-BF₃,²⁵ while HF-SbF₅ converts benzene (1) to the benzenium cation (2),²⁶ although benzene is a base 10⁹ times weaker than mesitylene.²⁷

The degree of protonation of benzene (1) determines the distribution of 1 between a catalyst phase and the organic phase in the conversion of a paraffinic or naphthenic hydrocarbon fraction which contains small quantities of benzene. The amount of 2 present at equilibrium with 1 (eq 1) can be determined by ¹³C



NMR.²³ At temperatures above -100 °C the positional isomers of 2 interconvert rapidly, so that the ¹³C NMR spectrum exhibits one averaged signal. If the protonation-deprotonation equilibrium is also fast, the observed chemical shift is the weighted average of the shifts for 1 and 2, and the content of 2 can be calculated easily.

Previous literature data indicated that benzene is largely protonated in a sizeable excess of 1:1 HF-SbF₅.²⁶ We established that the ¹³C NMR chemical shift for that mixture can be used as the value of 2 in HF solutions. Moreover, we found that benzene is still virtually completely protonated in a 30:1 HF-SbF₅ mixture, which should be weaker than the 1:1 acid,²⁸ and for an SbF₅ to benzene ratio of 3. By contrast, benzene is only 55% protonated in HF-TaF₅ at the same ratio of reactants (30:1:0.33) and 68% protonated for an HF:TaF₅:benzene ratio of 4.2:1:0.4.²³

The acidity of HF-SbF₅ had been determined by the Hammett indicator method, or by various NMR techniques, for a wide range of SbF₅ concentrations.^{24,28} The low solubility of TaF₅ in HF in the absence of carbocation precursors prevented similar measurements for HF-TaF₅ in the range of TaF₅ concentrations recommended for utilization as a catalyst. Benzene proton-

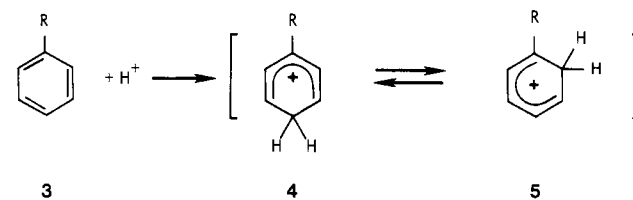
ation allowed a practical estimation which was then confirmed by extraction experiments.²⁹ In another study, it was found that a tertiary carbocation precursor is fully ionized in HF-TaF₅ at a reactant ratio of 30:1:0.33. It follows that benzene protonation requires a stronger acidity than formation of tertiary alkyl cations.³⁰ Benzene protonation can be used for acidity measurements on other acids for which traditional methods^{24a} are difficult to apply.

An important catalyst system for which we found no previous acidity estimates was aluminum bromide. It was known that for catalytic activity, small amounts of cocatalysts, like water or hydrogen bromide, are needed.³¹ A liquid or "sludge" catalytic phase is usually generated, containing AlBr₃, cocatalyst, and some organic material.³² The actual catalyst is, therefore, an HBr-AlBr₃ solution. We found that the HBr-AlBr₃ system completely protonates benzene at AlBr₃/benzene ratios of 2 or higher (2·Al₂Br₇).^{33,34} This establishes the HBr-AlBr₃ system as a powerful superacidic system. It is definitely stronger than HF-TaF₅, being in this respect similar to HF-SbF₅.³⁵

From the basicity difference between benzene and toluene,²⁷ one can predict that in a 30:1:0.33 mixture of HF-TaF₅-monoalkylbenzene, the latter is over 99.8% protonated. Yet, the difference in protonating ability of HF-SbF₅ and HF-TaF₅ manifests itself in a different behavior of monoalkylbenzenes (3) in these two media. We made a number of interesting observations by studying the protonation of 3 in both of these superacids.²³

Orientation of Protonation in Mono- and Dialkylbenzenes

Protonation of monoalkylbenzenes (3) is expected to occur mostly ortho/para. Indeed, the IR spectrum of



a. R = Me; b. R = Et

a "frozen" GaCl₃-HCl-toluene (3a) complex was interpreted as that of a mixture of para-(4a) and ortho-protonated (5a) isomers,²⁰ while decomposition of the solid complex of 3a, BF₃, and DF gave ortho- and para-deuterated toluene.^{14b} Also, examination of the ¹H NMR spectrum of 3a in HF-SbF₅-SO₂ solutions at -70 °C suggested that 4a and 5a were present in com-

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(29) Benzene (2.5-5% in the feed) is distributed between a hydrocarbon (alkane, cycloalkane) layer and HF-TaF₅, but it is fully extracted in HF-SbF₅ (studies by G. R. Chludzinski, in these laboratories).

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(34) Under HBr pressure, the superacid solution is approximately 4:1 HBr-AlBr₃.

(35) A comparison of HF-SbF₅ and HBr-AlBr₃ at the same HX:MX_n benzene ratios was not made, so far; therefore we cannot assess the possible difference in acidities between these two systems.

parable amounts.³⁶ It was later found that toluene reacts with SO₂ in these conditions, as does benzene, and the spectrum observed³⁶ had been that of protonated toluenesulfonic acids.³⁷

Reinvestigation of the protonation of toluene (**3a**) and ethylbenzene (**3b**) in the absence of SO₂ indicated that the para isomer (**4**) was the only product in each case.^{26b,38} A careful investigation by ¹H NMR indicated that no measurable amount of **5a** was present at equilibrium with **4a** at -100 °C.³⁹ This was at variance with the small reactivity difference between the two positions in the acid-catalyzed hydrogen isotope exchange.⁴⁰ One could, of course, rationalize this discrepancy as reflecting the difference between the thermodynamic and kinetic basicities of the two positions.⁴¹ In other words, there would be a large energy difference between the σ -complexes **4** and **5** but a small energy difference between the transition states preceding them along the reaction coordinates for the para and ortho protonation of **3**. Such a difference could have interesting consequences for the mechanistic representation of the aromatic protonation:^{14a} the transition state for para protonation could be closer to the π complex than the transition state for ortho protonation.^{14a,42} Some confusion was subsequently manifested, especially in theoretical papers. Some authors, on the basis of the superacid results,^{38,39} assumed that alkylbenzenes are protonated exclusively in the para position, under all conditions.⁴³ Others retained the viewpoint based on hydrogen exchange experiments, that ortho and para reactivities are not very different, even for equilibrium protonation.⁴⁴ Finally, others noticed the discrepancy between superacid and hydrogen-exchange experiments and sought an explanation for it.⁴⁵

On studying the protonation of ethylbenzene (**3b**) in HF-TaF₅ (30:1:0.33) by ¹³C NMR, we noticed peak broadening around -60 °C and then coalescence at higher temperature. The chemical shift changes were incompatible with exchange between **3b** and **4b**. Moreover, the solution in HF-SbF₅ exhibited the same changes in its spectrum above -10 °C. At temperatures where the exchange is fast (+10 °C), the spectra for the two solutions were the same, which again precluded the equilibrium **3b** \rightleftharpoons **4b** and indicated the equilibrium **4b** \rightleftharpoons **5b** as the cause for the observed exchange process.⁴⁶ It also indicated that the site of protonation (ratio of

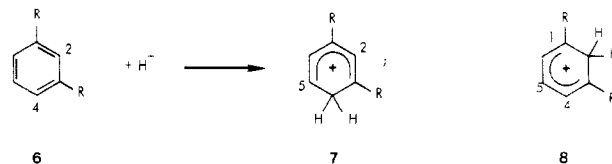
positional isomers) is not influenced by the acidic strength of the solution. The signals for **5b** could be seen at low temperatures at the locations expected based on the spectra at higher temperatures and on the spectra for protonated *m*-diethylbenzene.^{38,46} The **4b/5b** ratio was determined at low temperature by integration and at higher temperature from the chemical shifts of the averaged signals. An enthalpy difference close to -1 kcal/mol and an entropy difference in the range of -2 ± 1 eu were calculated for the interconversion **5b** \rightleftharpoons **4b**.⁴⁶ The ΔH° value is very close to the prediction based on additivity of substituent effects^{44b} while ΔS° is mainly the result of symmetry differences between **5** and **4**.

For toluene (**3a**) poorer solubility reduced the temperature range of the investigation, but for the interval of -10 to +10 °C the **4a/5a** ratios appeared very similar to those found for **3b**.⁴⁶

The **4/5** ratios at 0 °C (3-4) and +50° (ca. 2) are close to the reactivity ratio for the hydrogen exchange (1.3 at 70 °C).⁴⁰ This finding agrees with the usual representation of the electrophilic aromatic substitution, since the relative stabilities of the transition states parallel closely the relative stabilities of the corresponding σ complexes.

The difference in rates of interconversion of isomers, **4** \rightleftharpoons **5**, observed in HF-TaF₅ and HF-SbF₅ (coalescence temperature -30 and 0 °C, respectively) has mechanistic significance. It indicates that the exchange process is intermolecular, probably involving unprotonated alkylbenzene present in solution,²⁵ albeit in very small quantities (as mentioned above, monoalkylbenzenes are over 99.8% protonated in HF-TaF₅). It is, of course, possible that the mechanism is different in two cases, intermolecular in HF-TaF₅, but intramolecular in the stronger acid, HF-SbF₅.⁴⁶

Protonation of 1,3-dialkylbenzenes (**6**) in superacids was described to give the 4-protonated isomer (**7**).^{36,38,47} On the other hand, a paper on the sequential deuterium exchange of substituted benzenes by protonation with D₂O/D₃O⁺ in the ion cyclotron resonance (ICR) spectrometer reported that *m*-xylene (**6a**) exchanged only one hydrogen while toluene exchanged five and *p*-xylene exchanged four.⁴⁸ Since protonation to form **7a** should result in exchange at C-4 and C-6 with equal ease, one might conclude that in the conditions of the ICR experiment **6a** forms preferentially the 2-protonated isomer (**8a**). Subsequently, ab initio calculations indicated



that indeed position 2 in **6a** should be protonated preferentially.⁴⁹

We wanted to test whether these divergent results can be explained by the difference in temperature (-60 to

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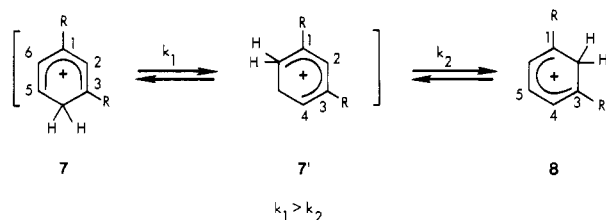
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90 °C for the superacid experiments^{36,38,47} and room temperature or higher for ICR).⁴⁸ The variable-temperature ¹³C NMR spectrum of protonated *m*-xylene and *m*-diethylbenzene (existing largely as the 4-protonated isomer, 7^{36,38,47}) evidenced two different exchange processes. The first was already apparent below 0 °C and did not affect the signal for C-2.⁵⁰ This was obviously due to the degenerate process 7 ⇌ 7'. At



a. R = Me; b. R = Et

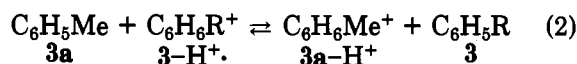
higher temperatures, the signal for C-2 broadened, and then sharpened again above 80 °C. This slower exchange process was identified as the rearrangement 7 ⇌ 8.^{51,52} We were then able to identify the signals for 8a and 8b at the expected locations in the ¹³C NMR spectra of protonated 6a and 6b, at -60 °C. Using the same approach as for the determination of the ortho/para ratios in the protonation of 3, namely, integration at low temperature (-60 °C) and chemical shifts at higher temperature (+80 to +95 °C), we determined the ratio 7/8 (30-40 at -60 °C, 12-14 at +90 °C) and the thermodynamic parameters for the equilibrium 8 ⇌ 7: $\Delta H^\circ = -1.0 \pm 0.4$ kcal/mol, $\Delta S^\circ = +2.3 \pm 1.3$ eu. The values are the same for protonated *m*-xylene as for protonated *m*-diethylbenzene.⁵¹

Our results ruled out the temperature difference as the source of the perceived⁴⁹ discrepancy between gas phase⁴⁸ and superacid studies.^{36,38,47} Another possible explanation is a site-specific solvation present in superacid solutions, favoring 7 over 8, which should be intrinsically more stable. However, a site-specific solvation should be sensitive to the size of alkyl groups, in disagreement with the identical isomer ratio observed for the protonated 6a and 6b, respectively. Also, the ΔS° values for the isomerizations 5 ⇌ 4 and 8 ⇌ 7 are small, their values and signs being in each case reasonably accounted for by the symmetry difference between isomers.⁵¹ As was pointed out before,⁵³ these ΔS° values are not consistent with specific solvation or ion pairing. It is more probable that in the gas phase protonation also occurs in position 4. However, the high basicity of *m*-xylene slows down very much the proton loss from 7, which is necessary in order to observe multiple exchanges. Since an ion suffers a limited number of collisions before it is analyzed, the very slow deprotonation is the reason for the single H/D exchange observed.⁵⁴ Indeed, more advanced exchange in *m*-

xylene was observed in a recent experiment of gas-phase ion-molecule exchange under positive ion chemical ionization conditions when D₂O was replaced by EtOD as the reagent gas.⁵⁵ The latter is more basic and therefore the rate of deprotonation of 7 should be higher than for D₂O. In light of these results,^{51,55} the ab initio calculations⁴⁹ should be viewed with some skepticism.

Relative Strength of Directing Effects of Methyl and Ethyl Groups on Protonation of the Benzene Ring

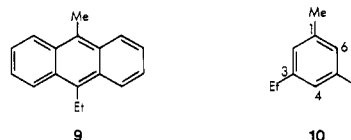
The relative ability of different alkyl groups to stabilize a protonated aromatic has been considered before. From a calorimetric study it was found that the proton transfer to toluene (3a) from protonated higher alkylbenzenes (eq 2) is exothermic, and the exothermicity



b, R = Et; c, R = *i*-Pr; d, R = *t*-Bu

increases in the series R = Et (3b) < *i*-Pr (3c) < *t*-Bu (3d).⁵⁶ While the values for 3c and 3d might have been affected by dealkylation⁵⁷ and disproportionation, the difference between the methyl and ethyl groups is still significant (2.84 kcal/mol^{56b}) and indicates that the methyl group better stabilizes the protonated form 3-H⁺.

A subsequent ICR study showed that in the gas phase the relative stabilities are in the opposite direction: the ethyl group stabilizes the protonated form better and eq 2 is endothermic by about 1 kcal/mol.^{43a,58} It is known, however, that in the gas phase the larger ions are generally favored.⁵⁹ To avoid this bias, an intramolecular competition for a proton between a site activated by a methyl group and a site activated by an ethyl group has been proposed. In one investigation, 9-methyl-10-ethylanthracene (9) was used as a sub-



strate. Protonation para to the methyl group was favored over protonation para to the ethyl group by a factor of 7.5 at -20 °C.⁶⁰ In a simpler system, 1,3-dimethyl-5-ethylbenzene (10), there is a much smaller difference. The ethyl group is marginally favored, since there is slightly less protonation in position 4 (para to methyl) than in position 2 (para to ethyl); the ratio is 0.85 at -40 °C.⁶¹ The study of 10 was based on the assumption that both methyl and ethyl groups in

(50) Actually, the exchange is clearly discernible at -20 °C. In contrast, the ¹H NMR spectrum of 7 was reported to show no indication of temperature dependence between -90 and -10 °C: Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* 1972, 94, 9241.

(51) (a) Fărcașiu, D.; *J. Chem. Soc., Chem. Commun.* 1982, in press. (b) Fărcașiu, D.; Melchior, M. T.; Kastrup, R. V., unpublished results.

(52) The averaged signal for C₄ and C₆ at +95 °C is shifted downfield from the average position in 7, by almost 2 ppm, again as predicted for 7 = 8. The signal for C-5 is virtually unaffected between -60 and +95 °C.

(53) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* 1973, 6, 53.

(54) My perception of this topic has benefited from discussions with J. L. Beauchamp.

(55) Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* 1980, 102, 6953.

(56) (a) Arnett, E. M.; Larsen, J. W. *J. Am. Chem. Soc.* 1969, 91, 1438;

(b) Arnett, E. M.; Abboud, J. L. M. *Ibid.* 1975, 97, 3865.

(57) (a) Brouwer, D. M. *Recl. Trav. Chim. Pays-Bas* 1968, 87, 210. (b)

Olah, G. A.; Mo, Y. K. *J. Org. Chem.* 1973, 38, 3221.

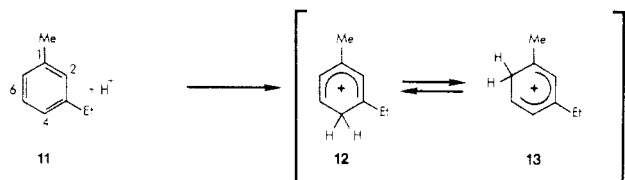
(58) (a) Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* 1976, 98, 7452. (b)

However, the reactivity sequence 3a > 3b > 3c > 1 was reported for the reaction with Me⁺ or Ph⁺ in the gas phase: Nefedov, V. D.; Sinotova, E. N.; Shishkunov, V. A. *Zh. Org. Khim.* 1976, 12, 1491, 1495.

(59) (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. "Energetics of Gaseous Ions", *J. Phys. Chem. Ref. Data* 1977, 6, Suppl. 1. (b) Meot-Ner, M.; Solomon, J. J.; Field, F. H. *J. Am. Chem. Soc.* 1976, 98, 1025 and references therein.

(60) Brouwer, D. M.; van Doorn, J. A. *Recl. Trav. Chim. Pays-Bas* 1970, 89, 88.

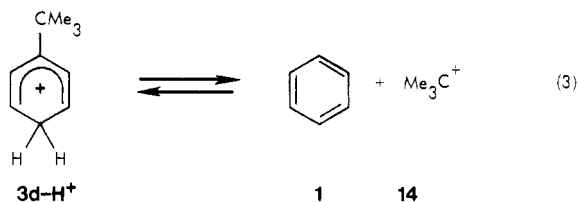
benzene direct protonation exclusively into the para position.^{39,61} This statement is not correct, but since the ortho/para ratio is about the same for the two substituents,⁴⁶ the errors are small. On the other hand, the protonation of **9** is probably affected by steric effects (protonation relieves peri interactions), as recognized by the original authors.⁶⁰ Such effects can be quite large in some cases.⁶² It was not established, however, whether some steric effects intervene in the protonation of **10** as well. If there are any such interactions in **10** they should be smaller or absent in the lower homologue, 3-ethyltoluene (**11**), which as we found forms on protonation equal amounts of **12** and **13**.^{51b} Taken together, the results in **10** and **11** establish



that the methyl and ethyl groups are equally effective in stabilizing protonated aromatics. This is noteworthy because it has been considered that replacement of a β -C-H by a β -CH₃ in carbocations should stabilize the systems, or in other words, that C-C hyperconjugation should be more effective than C-H hyperconjugation.⁶³

Position of the Dealkylation/Realkylation Equilibrium for Protonated *tert*-Alkylbenzenes

Attempts at protonating *tert*-butylbenzene (**3d**) or other *tert*-butyl-substituted aromatics in superacids (HF-SbF₅, FSO₃H-SbF₅) resulted in complete dealkylation, with the formation of *tert*-butyl cations (**14**).⁵⁷ Reaction of **3d** in superacid has been recommended as a convenient method for the preparation of **14**.^{57a} These observations suggested that the dealkylation equilibrium (eq 3) is fully displaced to the right. Since al-

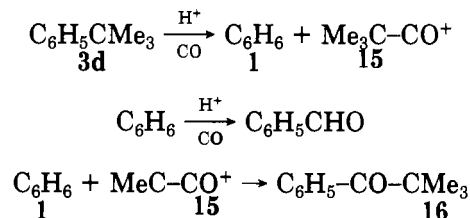


kylation-dealkylation reactions might play a role in the isomerization of alkanes in the presence of small amounts of benzene,^{22a} we investigated the protonation of **3d** in HF-TaF₅ as well.^{23,30} We found no dealkylation to **14**, however, although the NMR spectra indicated complete protonation, as for other monoalkylbenzenes (**3**).^{46,64}

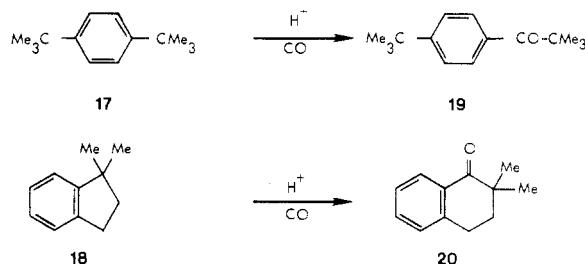
The complete dealkylation of **3d-H**⁺ observed by previous investigators does not actually reflect the position of the equilibrium in eq 3. Benzene, produced

by dealkylation, is fully protonated (eq 1)³³ in the stronger superacids employed in those studies,⁵⁷ thus displacing equilibrium 3 toward dealkylation. The acidity of HF-TaF₅, however, is high enough to stabilize *tert*-alkyl cations³⁰ and to fully protonate monoalkylbenzenes,⁴⁶ yet not sufficiently high so as to protonate benzene completely.³³

Equilibrium 3 can also be displaced to the right by reaction with CO,⁶⁵ which traps ion **14** as pivaloyl cations (**15**) and, more slowly, benzene as protonated benzaldehyde.⁶⁶ The acyl cation reacts in part with benzene to form pivalophenone (**16**).³⁰ The sequence

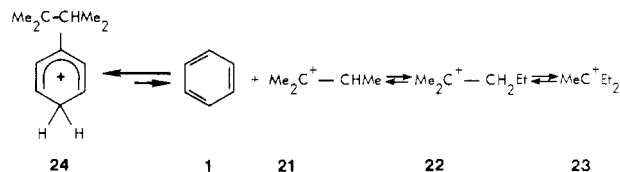


dealkylation, reaction with CO, and acylation amounts to a CO insertion into a tertiary alkylbenzene. We have shown that such CO insertions, catalyzed by HCl-AlCl₃ or HF-TaF₅, can in some cases be achieved in high yields, as shown below for *p*-di-*tert*-butylbenzene (**17**) and 1,1-dimethylindan (**18**), which form *p*-*tert*-butylpivalophenone (**19**) and 2,2-dimethyltetralone (**20**), respectively.⁶⁷



Reaction of Hexyl Cations with Benzene. Degradation of Higher Alkylbenzenes in Superacids

When a *tert*-alkylbenzene containing a larger alkyl group was protonated in HF-TaF₅, a more complicated reaction took place.⁶⁸ The alkylation-dealkylation equilibrium was quickly established upon protonation; the same results were obtained on treatment of an equilibrating mixture of *tert*-hexyl cation (**21-23**)^{57a} with benzene as on protonation of 1,1,2-trimethylpropylbenzene (**24**). A hydride transfer from the side chain



(61) Repinskaya, I. B.; Rezvukhin, A. I.; Koptuyg, V. A. *Zh. Org. Khim.* 1971, 7, 2143.

(62) Hart, H.; Jiang, J. B.-C.; Gupta, R. K. *Tetrahedron Lett.* 1975, 4639.

(63) (a) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1972, 94, 5935. (b) For results suggesting the opposite conclusion, see: Jones, A. J.; Huang, E.; Haseltine, R.; Sorensen, T. S. *Ibid.* 1975, 97, 1133.

(64) The para-protonated isomer is written here as the structure for **3d-H**⁺. The occurrence of some ortho-protonated material (**5d**) at equilibrium is possible, but was not investigated. Dealkylation actually involves the ipso-protonated isomer as an intermediate.

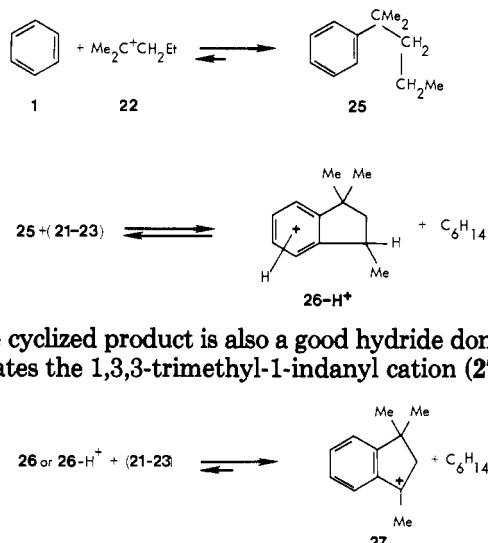
(65) For a review on the reaction of carbocations with CO, see: Hogeveen, H. *Adv. Phys. Org. Chem.* 1973, 10, 29.

(66) Gattermann-Koch reaction; for a review see: Olah, G. A.; Kuhn, S. J. in ref 1b, Vol. 3, 1964, p 1153.

(67) Fărcașiu, D.; Schlosberg, R. H. *J. Org. Chem.* 1982, 47, 151.

(68) (a) Fărcașiu, D.; Siskin, M.; Rhodes, R. P. "Abstracts of Papers", 176th National Meeting of the American Chemical Society, Miami Beach, FL, Sept 15, 1978; American Chemical Society: Washington, D.C., 1978; ORGN-153. (b) Fărcașiu, D.; Siskin, M.; Rhodes, R. P. *J. Am. Chem. Soc.*, 1979, 101, 7671.

of **24**, or more probably from the side chain of its isomer, **25**, to the hexyl cations (**21–23**) present at equilibrium in very small quantities takes place in these conditions, generating a phenylhexyl cation, which undergoes cyclization to an indan derivative, **26**, in its protonated form.



The cyclized product is also a good hydride donor and generates the 1,3,3-trimethyl-1-indanyl cation (**27**). As

a result, **24** (or the mixture of **1** and **21–23**) is more than 90% converted to **27**, hexanes, and benzene, in a short time. On longer standing, **27** rearranges partially to a more complex mixture of indan and Tetralin derivatives.⁶⁸ The formation of **27** is reversible. When **27** was treated with an excess of pentane/isopentane (hydride donor), benzene was isolated.

Superimposed over this reversible transformation is a slow degradation process, which leads to formation and accumulation of protonated ethylbenzene (**28**) in solution. The overall picture derived from these experiments is summarized in Chart I.

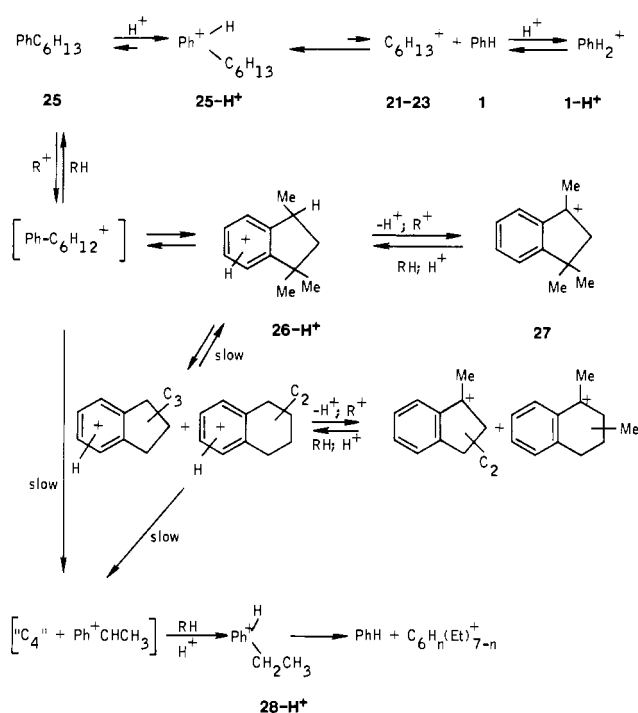
Generation of ethylbenzene (**28**) was observed in our laboratories in many acid-catalyzed hydrocarbon conversions run for long periods of time with feeds which contained at least traces of benzene. At even longer reaction times, **28** disproportionated to benzene and protonated polyethylbenzenes. The ethylbenzene (**28**) and polyethylbenzenes appear to be the ultimate degradation product from higher alkylbenzenes.⁶⁹ The best way to regenerate a catalyst containing these species is probably by quenching and extraction, followed by dehydration.⁷⁰ For a superacid stronger than HF-TaF_5 , for example, HF-SbF_5 , benzene is fully protonated,³³ and as such it is fully extracted from a hydrocarbon layer.²⁹ Accumulation of benzene occurs until the acidity of the system decreases, after which the same kind of degradation as described above can be expected. In the case of HF-SbF_5 , however, the picture is complicated by the oxidizing nature of SbF_5 , which becomes more apparent as the ratio of SbF_5 to aromatics decreases.³³

In summary, our work has helped clarify some basic questions concerning protonation of alkylbenzenes. The

(69) In the Friedel-Crafts methylation and ethylation of benzene, the final alkylation products, which totally deactivate the catalyst, are heptamethylbenzenium⁷ and heptaethylbenzenium³⁸ salts, respectively.

(70) Kim, C. J.; Fărcașiu, D., U.S. Patent 4124692, 1978.

Chart I



study of benzene protonation has invalidated the erroneous viewpoint that HBr-AlBr_3 is weaker than the "superacids", which consist of heavy metal fluorides (SbF_5 , AsF_5 , TaF_5 , NbF_5 , BiF_5) in HF .^{24b,71} Determination of ortho/para ratios for protonated monoalkylbenzenes has eliminated the apparent discrepancy between thermodynamic and kinetic relative basicities of these sites. Together with the study on the site of protonation of 1,3-dialkylbenzenes, these measurements have indicated the absence of site-specific solvation for the corresponding ions. Weaknesses of some theoretical treatments that rationalized experimental results proven erroneous have been uncovered. The equality of the activating effect of methyl and ethyl groups competing on the same molecule, in the absence of steric interactions, has indicated the equivalence of $\beta\text{-C-C}$ and $\beta\text{-C-H}$ bonds in these systems. The protonated *tert*-alkylbenzenes have been shown to dealkylate reversibly, but the equilibrium is displaced toward the alkylated material. Our work has also elucidated the mechanism of deactivation of superacid catalysts by traces of benzene present in the saturated hydrocarbon feeds.

Much of my work was done in collaboration with my colleagues: Drs. M. Siskin, R. L. Hartgerink, R. H. Schlosberg, R. P. Rhodes, C. J. Kim, R. Hulme, G. R. Chludzinski, and J. Wristers. Analytical support was provided by Drs. M. T. Melchior, R. V. Kastrup, and K. D. Rose (NMR), T. Ashe, and C. S. Hsu (M.S.), and W. E. Tyler, III (GLC), and their staffs. My co-workers, L. P. Craine, J. J. O'Donnel, S. L. Fisk, and C. P. Pearce, are thanked for their essential contribution. Last, but not least, many discussions with Professors H. C. Brown, R. J. Gillespie, and R. Pettit are gratefully acknowledged.

(71) Recently it was stated: "It is ... not surprising that by the use of strong acids ... such as TaF_5/HF ... which are 10^2 ... times stronger than AlX_3/HX , a new magnitude to catalytic reactions was uncovered" (Pines, H. "The Chemistry of Catalytic Hydrocarbon Conversions"; Academic Press: New York, 1981; p 95).