The failure of eq 19 at the lower acid concentrations is illustrated in Table VI. In the first two columns of that table, experimental values of $1/\tau$ are compared with calculations of $k_+/(1 + k_-[\text{HTS}]/k_e)$, using rate constants obtained at the higher acid concentrations according to (21). The discrepancy between the two columns increases with decreasing [HTs] and becomes highly significant below $5 \times 10^{-4} M$.

Table VI. Fit of Eq 18 to Data for N,N-Diethylanilinium *p*-Toluenesulfonate at 26°

$1/\tau$, sec^{-1}	$k_+/(1 + k_-[\text{HTs}]/k_e)$ sec^{-1}	10^3[HTs], M	[BH$^+$Ts$^-$], M	kK
281	257	1.522	0.104	7.9
744	492	0.556	0.110	(13)[a]
932	581	0.395	0.110	7.7
1102	625	0.332	0.112	7.9
1243	677	0.268	0.110	5.9
1735	768	0.178	0.107	5.3
2150	828	0.128	0.105	4.3
2980	902	(0.076)[b]	0.103	(3.2)[a]
750	596	0.372	0.056	3.8
1150	694	0.249	0.056	6.7
1460	742	0.201	0.056	8.3

[a] Omitted from average. [b] Outside the range in which [HTs] can be measured with good accuracy.

The final column of Table VI shows the extent to which inclusion of ion-pair exchange in the rate law succeeds in fitting the data. Using the values of k_e, k_+, and k_- obtained at the higher acid concentrations, we have calculated the parameter kK for each experimental point, using eq 18. The values obtained in this way are fairly constant and the scatter could be random. What is more significant, Table V shows that average values obtained in the series with 0.11 M BH$^+$Ts$^-$ and with 0.056 M BH$^+$Ts$^-$ are almost exactly equal. This is to say, the kinetics of interconversion of BH$^+$Ts$^-$ and BH$^+$Ac$^-$ by this mechanism is, on the average, consistent with that for ion-pair exchange.

Alternatives to BH$^+$Ac$^-$ As the Reactive Intermediate. We have seen that a reaction mechanism involving BH$^+$Ac$^-$ as the reactive intermediate can accommodate all facts. We now wish to show that there are few if any alternatives.

One constraint is imposed by the kinetics. The fact that the rate becomes proportional to [BH$^+$Ts$^-$]/[HTs] at the higher acid concentrations implies that the molecular formula of the intermediate is [BH$^+$Ts$^-$ − HTs + nHAc]; that is, the intermediate must be either solvated BH$^+$Ac$^-$ or solvated B or a subspecies or isomer of these species. The other constraint is imposed by the rate itself. For definiteness, consider the rate constant, k_-, for the reaction of the intermediate with HTs to form BH$^+$Ts$^-$, and suppose that k_- is obtained by a graphical method based on eq 21, that is, $k_- = (\text{intercept})^2/(\text{slope}\cdot K)$. Intercept and slope are defined by the kinetic data, but K is the equilibrium constant for the formation of the intermediate, and its value will depend on the particular species we propose for the intermediate. If we modify our theory so as to make the intermediate less stable, K will decrease and k_- will increase. But k_- cannot be larger than the encounter frequency of the intermediate with HTs and should certainly be less than 10^{11} sec^{-1} M^{-1}. If we assume that the intermediate is BH$^+$Ac$^-$, k_- turns out to be 10^{10} sec^{-1} M^{-1}. We conclude, therefore, that any intermediate we propose must be so stable that its concentration is at least one-tenth as great as that of solvated BH$^+$Ac$^-$. This constraints rules out all mechanisms that propose solvated B or any of its subspecies for the intermediate (see K_i values in Table I).

Reactions of He^{3}H$^+$ Ions with Gaseous Hydrocarbons.
I. Toluene

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Abstract: The gas-phase reaction of the He^{3}H$^+$ ions from the decay of molecular tritium with toluene was investigated under conditions ensuring that the labeled decay fragments were the only source of tritiated products, with no significant interference from radiolytic processes. The reaction responsible for the formation of tritiated toluene, the major product isolated with a yield of 50 to 60%, appears to be similar to the electrophilic aromatic substitutions occurring in solution, as indicated by experiments involving the competition for the He^{3}H$^+$ ions between toluene and benzene, and benzene and α-trifluorotoluene, and by the analysis of the isomeric distribution of the tritiated toluenes formed. The mechanisms responsible for the formation of the two other products identified, *i.e.*, labeled methane and benzene, are also discussed.

The existence of the singly charged helium hydride molecular ion HeH$^+$ has been known for many years by mass spectrometric investigations,[1] and several quantum mechanical calculations for the ground state of this very simple two-electrons heteronuclear system were

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[1] T. R. Hogness and E. C. Lunn, *Phys. Rev.*, **26**, 44 (1925).

published.[2,3] From the point of view of its chemical reactivity, the results of such investigation confirmed what could be expected from the very nature of this exceedingly strong Brønsted acid, *i.e.*, its ability to exothermically protonate any organic compound.

In recent years, a remarkable series of investigations on the decay of tritium hydride and molecular tritium renewed interest in the HeH^+ and He^3H^+ ions and indicated a simple and convenient way for their preparation. In fact, the calculations by Cantwell[4] and Schwartz,[5] and the experimental investigations by Snell, *et al.*,[6] and Wexler,[7] demonstrated that HeH^+ and He^3H^+ ions are produced in the ground state in over 90% of the β decays of tritium hydride and, respectively, molecular tritium. These results leave little doubt that the nuclear decay of molecular tritium affords a unique means to produce, within any organic system at any pressure, an extremely powerful protonating reagent of unusually well-defined nature, and to identify by tracer techniques the products formed from its reactions with the organic substrate.

It appears that the use of He^3H^+ decay ions has not yet received the interest it deserves as a method of studying, in both aromatic and aliphatic systems, gas-phase electrophilic reactions of considerable interest to the physical organic chemist. The reactions promoted by the decay of $^3H_2$ in the presence of a variety of organic molecules were the object of intensive investigations, in connection with a most useful and widely used labeling technique, introduced by Wilzbach[8] in 1957.

The Wilzbach method consisted of mixing the organic compound with several curies of $^3H_2$ and allowing the system to stand for a few days. On analyzing the various labeled products formed, Wilzbach observed that a number of radioactive compounds were produced, in addition to the tritiated parent. Apart from its preparative applications, the Wilzbach labeling method was the subject of a series of investigations to determine the mechanism responsible for the formation of the tritiated products.

Riesz and Wilzbach,[9] reporting in 1958 on the labeling of C_6 hydrocarbons by exposure to $^3H_2$, suggested that two basic modes of labeling were operative: the reactions of the tritiated species from the decay of $^3H_2$, which they called the "recoil triton," and radiolytic processes initiated by the tritium β particles. Between 1959 and 1962 Gant and Yang reported the results of a series of investigations on the contribution of the different labeling modes to the formation of the tritiated products obtained from the exposure of ethane,[10] ethylene,[11] cyclopropane,[12] and propane[13] to several curies of $^3H_2$. Their study, involving such techniques as the replacement of tritium with hydrogen tritide, the irradiation of the system with an external γ-ray source, and the use of radical scavengers, confirmed that the labeling occurred *via* two different processes, initiated, respectively, by He^3H^+ ions and by the decay electrons.

Perhaps the sharpest focus to the problem concerning the separation of the various labeling modes was brought by the work of Pratt and Wolfgang[14] on the methane–tritium system. From a careful kinetic analysis, including the use of suitable radical scavengers, Pratt and Wolfgang concluded that three modes of labeling are operative, involving respectively the reactions of the He^3H^+ ions, the radiolytic processes initiated by the action of the β particles on the tritium, and the radiolytic processes initiated by the action of the β particles on the methane. Pratt and Wolfgang also presented a quantitative evaluation of the relative weights of the different labeling modes for a gaseous system and discussed the possible mechanisms responsible for the formation of the observed tritiated products. A completely different approach, involving the use of a special mass spectrometer, was employed by Wexler,[15] who in 1962 reported on the exchange of $^3H_2$ with methane. Again, the formation of the charged tritiated species observed in the mass spectrometer was ascribed to two basic labeling modes, involving, respectively, the reactions of the decay He^3H^+ ions and the radiolytic processes promoted by the tritium decay electrons.

The application of the Wilzbach technique to aromatic compounds was also the subject of a number of investigations, usually involving the measurement of the intramolecular tritium distribution within the labeled aromatic substance. While most workers employed toluene as the aromatic substratc,[16-21] chlorobenzene, nitrobenzene, and anisole[22] were also studied.

As a whole, the investigations cited in both aliphatic and aromatic systems provide a consistent and satisfactory picture of the different physical processes which promote the formation of the tritiated products and their relative weights in the Wilzbach labeling method. It appears, however, that the situation is less satisfactory from the point of view of a detailed, mechanistic analysis of the chemical reactions of the He^3H^+ ions. In fact, owing to the high activity of the $^3H_2$ employed, the systems studied almost invariably received a large dose of radiations, and the labeled products from the reactions of the He^3H^+ ions were largely obscured by the spectrum of tritiated products arising from radiolytic processes. Under such conditions, the nuclear decay of $^3H_2$ obviously cannot afford a satisfactory means of production of the protonating reagent He^3H^+, in the gas phase.

While some information on the extent of the radiolytic processes can certainly be provided by indirect tech-

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(2) For a review of theoretical calculations on the HeH^+ ions, *cf.* H. H. Michels, *J. Chem. Phys.*, **44**, 3834 (1966).

(3) L. Wolniewicz, *ibid.*, 43, 1087 (1965).

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(12) P. L. Gant and K. Yang, *ibid.*, 32, 1757 (1960).

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(16) B. Aliprandi, F. Cacace, and L. Cieri, *Ric. Sci.*, 30, 90 (1960).

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(19) F. Cacace, ref 18, p 133.

(20) H. J. Ache, W. Herr, and A. Thiemann, "Tritium in the Physical and Biological Sciences," Vol. II, International Atomic Energy Agency, Vienna, 1962, p 21.

(21) H. J. Ache and W. Herr, *Z. Naturforsch.*, **17a**, 631 (1962).

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niques, such as the irradiation with external γ sources, the use of radical scavengers, etc., there is no doubt that if the nuclear decay of tritium is to be used as a reliable method of studying gas-phase ionic reactions, the interference from radiolytic processes must be eliminated. Fortunately, the rate of formation of the He^3H^+ ions is proportional to the first power of the $^3H_2$ concentration, while the over-all rate of the radiolytic labeling reactions, where the tritium, in addition to being a reactant, is also the source of the radiation, must be proportional to a higher power of the $^3H_2$ concentration. It is therefore to be expected that, by drastically decreasing the concentration of $^3H_2$ in the system investigated, the tritiated products formed through radiolytic processes can be reduced to an insignificant fraction of those arising from the reactions of the decay ions.

In order to assess the usefulness of the technique based on the β decay of $^3H_2$ as a method of studying gas-phase ionic reactions, it was decided to undertake a comprehensive study of the proton-transfer processes between He^3H^+ ions and a variety of aromatic and aliphatic compounds, under conditions ensuring the elimination of any interference from radiolytic processes.

The present paper describes the results obtained in the study of the gas-phase reactions of the He^3H^+ ions with toluene.

Experimental Section

Materials. Tritium gas was obtained from CEA (France) with a stated purity greater than 95%, the main contaminant being ^3He. Since the purity of the $^3H_2$ was essential to the present investigation, the sample was subjected to a careful radio gas chromatographic analysis.

The isotopic composition was determined using an 8-m column, packed with activated alumina and operated at −196°, which provides a clean separation of the tritium from the hydrogen tritide.[23] The outlet of the column was connected to a 25-ml flow ionization chamber, whose current was measured with a Model 610 B electrometer of Keithley Instruments Inc. (Cleveland, Ohio), in order to obtain a continuous monitoring of the activity of the effluents. The analysis showed that the hydrogen tritide accounted for less than 2% of the $^3H_2$ activity. The tritium sample was further analyzed using a 3-m 5-A molecular sieves column, whose temperature was programmed from 80 to 240°, with a gradient of 10°/min in order to determine any lower tritiated hydrocarbon. The only impurity found was labeled methane, whose activity reached about 0.3% of the $^3H_2$ activity. Finally, an analysis carried out with a 6-m silica gel column, heated to 100°, failed to detect any tritiated hydrocarbon of higher molecular weight.

Hydrogen tritide was prepared by sparking a diluted solution of $^3H_2$ in H_2 with a Tesla coil and was analyzed as described for the tritium, in order to ascertain the completeness of the exchange reaction and the radiochemical purity of the sample.

The benzene and toluene were reagent grade chemicals from Merck (Darmstadt, Germany) and were used without further purification. Fully deuterated toluene, with a stated isotopic purity greater than 95%, was obtained from CEA (France).

The aromatic hydrocarbons were analyzed for possible impurities by gas chromatography, using a 3-m didecylphthalate column, heated to 110°. No detectable amount of benzene was found in both the light and heavy toluene.

The gaseous hydrocarbons used for identification purposes, *i.e.*, methane, ethane, ethylene, acetylene, propane, were purchased from Societá Rivoira (Torino, Italy). The helium used as the carrier gas in the chromatographic analyses was a product from Chemetron Co. (Chicago, Ill.).

Procedure. Preparation of the Sample. A weighed amount (*ca.* 10 mmoles) of the aromatic hydrocarbon was introduced into a 250-ml Pyrex vessel, sealed to a 10-ml ampoule, which contained *ca.* 1.7 mcuries of tritium gas (or hydrogen tritide), and closed by a fragile tip. The vessel was then connected to a vacuum line and its contents thoroughly outgassed by repeated pumping at the liquid nitrogen temperature.

The vessel was sealed off, under a vacuum better than 10^{-4} torr, and the fragile tip of the 10-ml ampoule was broken, thus allowing the $^3H_2$ to expand into the vessel before the aromatic hydrocarbon could melt. For the competition experiments, mixtures of benzene + toluene, and benzene + α-trifluorotoluene in different molar ratios were used, the total amount of aromatic compounds reaching again *ca.* 10 mmoles. For those runs requiring the presence of a radical scavenger, oxygen was introduced into the vessel just before sealing it off.

Growth and Analysis of the Labeled Products. The sealed vessels were stored in the dark for periods ranging from 1 to 3 months in a thermostatic oven, whose temperature was adjusted to 110°. At this temperature, the vapor pressure of the toluene reaches 760 torr and the whole sample vaporizes, forming a homogeneous gas phase and ensuring a complete mixing of the tritium with the aromatic hydrocarbon. After the necessary storage period, the vessels were cooled to room temperature and their contents were analyzed.

Two separate types of analysis were carried out on each sample, *i.e.*, the quantitative analysis of the labeled products formed from the reactions of the He^3H^+ ions, and the determination of the tritium distribution within the molecule of the labeled toluene. The products analysis was carried out by radio gas chromatography, using the same columns described in the previous section and monitoring the activity of the effluents with a 100-ml flow ionization chamber, whose current was measured with a Model 475A vibrating reed electrometer of the Victoreen Instrument Co. (Oak Lawn, Ill.). Full details on the radio gas chromatographic technique, which involves the heating of the ionization chamber to 110° to prevent the condensation of the higher boiling hydrocarbons, have been reported elsewhere.[24]

The determination of the intramolecular tritium distribution within the labeled toluene required the rigorous purification of the hydrocarbon and the preparation of a series of derivatives, where the hydrogen of a given position was replaced by a suitable inactive group.

The purification of the labeled toluene was accomplished by preparative gas chromatography, using a 3-m didecylphthalate column with an inner diameter of 6 mm, heated to 120°. A collection technique was employed that eliminates the possibility of a cross-contamination of the elution peaks by using separate glass tubes for the trapping of the individual fractions.[25]

The gas chromatographic purification step was repeated until the specific activity of the toluene reached a constant value. An aliquot of toluene was then nitrated with ethyl nitrate and $AlCl_3$. The isomeric nitrotoluenes formed were separated and purified by preparative gas chromatography on a 2-m Apiezon L column heated to 205°, and their specific activities were measured. Another aliquot of the purified toluene was oxidized with a neutral solution of potassium permanganate in a sealed tube at 120° to benzoic acid, which was in turn converted to its methyl ester with an ethereal solution of diazomethane. The methyl benzoate was purified by preparative gas chromatography, using a 2-m Apiezon L column, heated to 205°, and its specific activity was determined. In a few cases, part of benzoic acid was brominated with hypobromic acid and the *m*-bromobenzoic acid formed was treated with diazomethane in ether. The methyl *m*-bromobenzoate obtained was then purified by preparative gas chromatography at 210°, using the column employed for the methyl benzoate. The specific activity of the purified ester was also measured.

It may be worth mentioning that the substitution reactions employed involve no exchange of tritium between the labeled toluene and the solvent or the reagents, nor do they exhibit a $H/^3H$ isotope effect significant for the purposes of the present investigation, as indicated by previous work[20] or, when required, by suitable blank runs.

Specific Activity Measurements. The specific activity of the toluene and its derivatives was measured with a 250-ml static ionization chamber, after the quantitative conversion of the organic samples to a gaseous mixture of H_2 and CH_4 by the combustion method described by Wilzbach, Kaplan, and Brown.[26]

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(23) M. A. Smith and E. H. Carter, ref 20, Vol. I, p 121.

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Results

The per cent abundance of the charged fragments from the decay of molecular tritium, as measured by Wexler[7] by a mass spectrometric method, is shown in Table I. The $^3He^3H^+$ ion is by far the most abundant fragment, being formed in 94.5% of the β transitions. From the data of Table I, little doubt remains that, when the $^3H_2$ decay takes place at atmospheric pressure, the only fragment whose reactions need to be considered is the molecular ion He^3H^+.

Table I. Abundances[a] of the Ionic Fragments from the Decay of $^3H_2$

Fragment	% abundance
$^3H^+ + (^3He)^+$	5.5 ± 0.6
$(^3H^3He)^+$	94.5 ± 0.6

[a] Data taken from ref 7.

Table II summarizes the yields of the labeled products formed when $^3H_2$ is allowed to decay in the presence of light and deuterated toluene, both neat and containing 2 mole % of oxygen, used as a radical scavenger. The yield of any given product is the ratio of the activity found in that product to the total activity contained in the He^3H^+ ions formed within the system from the $^3H_2$ decay.

Table II. Yields of Labeled Products from the Decay of $^3H_2$ in Gaseous Toluene

Products	Yield,[a] %				
	$^3H_2 + C_7H_8$[b]	$^3H_2 + C_7D_8$	$^3H_2 + C_7H_8 + O_2$[c]	$^3H_2 + C_7D_8 + O_2$[c]	$^1H^3H + C_7H_8 + O_2$[c]
Toluene	49 ± 5	58 ± 6	60 ± 8	60 ± 8	Below detection limit[d]
Benzene	2.7 ± 0.5	3.6 ± 0.5	3.8 ± 0.5	3.6 ± 0.5	Below detection limit[d]
Methane[d]	*Ca.* 8	*Ca.* 10	...	*Ca.* 6%	...

[a] Fraction of the total activity of the decay He^3H^+ ions found in a given product. The data represent the mean value of at least four determinations, whose standard deviation is listed . [b] 10 mmoles of toluene and 1.7 mcuries of $^3H_2$ or $^1H^3H$ were employed in all the samples which were stored at 110° and atmospheric pressure. [c] The oxygen concentration was 2.0 mole %. [d] See text.

The most striking feature of Table II is the high yield of labeled toluene, ranging from *ca.* 50% in the system $C_7H_8 + {}^3H_2$ to *ca.* 60% in all the other systems. Owing to the errors affecting the measurements of the absolute yields (reflected by the relatively large standard deviation of the values listed in Table II), probably no particular meaning has to be attached to the somewhat lower yield of tritiated toluene found in the $C_7H_8 + {}^3H_2$ system. It is interesting to note that the yield of the labeled toluene is not reduced by the addition of oxygen as a radical scavenger. This indicates that thermal radicals are not involved in the processes responsible for the formation of labeled toluene, in agreement with the hypothesis that the tritiated hydrocarbon is produced from the reactions of a charged species, the He^3H^+ ion.

Tritiated benzene and methane were also found in the four systems analyzed, the combined yields of all the products identified ranging from 60 to 70%. It must be pointed out that the yields of methane listed in Table I are affected by an unusually high uncertainty, arising from the presence in the tritium gas used for the reaction of labeled methane, an impurity whose removal is very difficult according to Yang and Gant.[13] The yield was therefore determined by subtracting the initial content of labeled methane from the amount found after the reaction time; this is, of course, largely approximate.

In order to ascertain whether radiolytic processes play any role in the formation of the tritiated products, comparative runs were carried out where the molecular tritium was replaced by an equivalent activity of hydrogen tritide. Since the latter gives upon β decay the inactive HeH^+ ions, the formation of labeled products through the reactions of the decay ions is suppressed, and any tritiated compound observed necessarily arises from radiolytic processes. No labeled product, including toluene, was observed in the blank runs, while the analytical technique employed could detect activities of tritiated compounds down to a few per cent of those measured in the systems containing molecular tritium. Therefore, the hydrogen tritide runs provide a conclusive evidence that the radiolytic processes play no significant role in the formation of the labeled products under the experimental conditions employed in the present investigation. Furthermore, such experimental evidence is supported by considerations based on the amount of energy absorbed by the system during the storage period.

Competition experiments, based on the reactions of decay-formed He^3H^+ ions with gaseous mixtures of toluene + benzene, and benzene + α-trifluorotoluene, were carried out under the same conditions employed for pure toluene, in order to determine the relative rate of the He^3H^+ ions attack on these substrates. The yields of tritiated toluene, benzene, and α-trifluorotoluene, measured for different (1:10, 1:1, 10:1) molar ratios of the competing substrates, were corrected for the small amount of labeled benzene that had been previously found to arise from the reactions of the He^3H^+ ions with pure toluene and α-trifluorotoluene, and give the following relative rates: α-trifluorotoluene, 0.45 ± 0.05; benzene, 1.00; toluene, 2.10 ± 0.20.

Table III illustrates the intramolecular distribution of tritium within the molecule of the labeled toluene from the reaction of the He^3H^+ ions with C_7H_8 and C_7D_8, respectively, both neat and containing 2 mole % of O_2. The main features of the intramolecular tritium distribution can be summarized as follows: (i) most of the tritium (92 to 95%) is found in the ring positions; (ii) within the ring, the *ortho* and *para* positions are strongly preferred, accounting together for about 80% of the total activity; (iii) the distribution resulting from the He^3H^+ attack on C_7H_8 and C_7D_8 is substantially the same and appears to be insensitive to the presence of the radical scavenger.

Table III. Distribution of Tritium within the Molecule of Labeled Toluene

	Tritium content,[a] %			
Molecular positions	$^3H_2$ + C_7H_8	$^3H_2$ + C_7D_8	$^3H_2$ + C_7H_8 + O_2	$^3H_2$ + C_7D_8 + O_2
Each α position	2.3	2.7	1.9	2.7
Each *ortho* position	27	26	27	25
Each *para* position	22	24	23	23
Each *meta* position	8.6	8.0	8.8	9.5

[a] The percentages listed are the mean values obtained from several determinations. The standard deviation of the data is *ca.* 10%, except for the *meta* position, whose activity was determined in most cases by difference, which involved a larger standard deviation, of the order of 20%.

Discussion

Formation of the Tritiated Toluene. The data reported in the previous section, in particular the relative reactivity of toluene, benzene, and α-trifluorotoluene, as well as the distribution of the tritium within the molecule of the labeled toluene, are consistent with the hypothesis of an electrophilic attack of the aromatic compound by the He^3H^+ ions, whose exceedingly high reactivity provides a reasonable explanation of the low substrate and positional selectivity observed.

This interpretation is supported by reference to a number of low-selectivity electrophilic substitutions occurring in aprotic solvents and involving reactive electrophiles, such as carbonium ions.[27-34] In this connection, the close similarity between the substrate and positional selectivity that can be found between the results of the present investigation and those obtained by Jurewicz, Bayless, and Friedmann[35] in their study of the reactions of poorly solvated alkyl ions with aromatic hydrocarbons, under the conditions that most closely approach in the solution chemistry the environment where the reactions of the unsolvated, gaseous He^3H^+ ions take place, appears particularly meaningful.

A comparison with the data of Jurewicz, Bayless, and Friedmann shows that both reactions exhibit a very close substrate selectivity. As to the positional selectivity, while the percentages of the *meta* isomers are surprisingly close, the higher value for the *ortho* positions, and correspondingly the lower value for the *para* position found in the present investigation, is exactly what one should expect from the different steric requirements of the He^3H^+ ion *vs.* the isopropyl ion. On the grounds of such comparison, one is tempted to postulate that the mechanism of the attack by the He^3H^+ ions on the aromatic substrate is similar to the mechanism of the aromatic substitutions occurring in solution.

There is no doubt that the labeled ion formed from the decay of molecular tritium

$$^3H_2 \longrightarrow {}^3He^3H^+ + \beta^- \qquad (1)$$

is a strong Brønsted acid, which can be expected to readily protonate toluene and benzene through the exothermic processes

$$C_6H_6 + He^3H^+ \longrightarrow C_6H_6{}^3H^+ + He \qquad (2)$$

$$C_7H_8 + He^3H^+ \longrightarrow C_7H_8{}^3H^+ + He \qquad (3)$$

The heat of reaction for process 2 can be roughly estimated[14,36] to approach -100 kcal/mole. While the heat of formation of the protonated toluene is not known,[36] and ΔH for the reaction 3 cannot be therefore calculated, it is likely to exceed the value indicated for reaction 2.

The excited protonated ions can either decompose along energetically allowed fragmentation pathways or be deactivated by collision to produce stabilized $C_7H_8{}^3H^+$ ions that can be expected to react with the C_7H_8 to produce the observed labeled toluene, according to the thermoneutral proton-transfer process

$$C_7H_8{}^3H^+ + C_7H_8 \longrightarrow C_7H_7{}^3H + C_7H_9{}^+ \qquad (4)$$

analogous to those observed, for instance, between $CH_5{}^+$ and $C_2H_7{}^+$ ions and, respectively, methane and ethane.[37]

The stabilization of at least part of the $C_7H_8{}^3H^+$ ions from reaction 1 appears likely, despite their large excitation energy, since the reaction takes place in a system at atmospheric pressure, *i.e.*, under conditions that ensure a high efficiency of the collisional deactivation processes.

Furthermore, Munson and Field, in their mass spectrometric investigation on the interaction of $CH_5{}^+$ ions with a number of arenes,[36] have found that the protonated aromatic ions from the process

$$CH_5{}^+ + ArH \longrightarrow CH_4 + ArH_2{}^+ \qquad (5)$$

which is similar to reaction 3, can be observed in high yields at the pressure of 1 torr. While it could be argued that reaction 3 is considerably more exothermic than reaction 5, one should consider the much higher pressure prevailing in the present experiments and the fact that even simpler ions, with a considerably smaller number of internal degrees of freedom, have been often found to be effectively stabilized at a pressure of a few torr, despite their high excitation energy.

On the other hand, the dissociation of at least a fraction of the excited $C_7H_8{}^3H^+$ ions from reaction 1, for instance, into $C_7H_7{}^+$ ions and hydrogen tritide, could explain the finding that the combined yields of all the tritiated products identified account only for 60 to 70% of the activity originally contained in the He^3H^+ ions. In fact, the hydrogen tritide yield could not be measured in the present experiments, owing to its presence as a relatively abundant impurity in the $^3H_2$ used to produce He^3H^+ ions.

Some information on the nature of the protonated intermediate formed in reaction 3 can be obtained from the distribution of the tritium within the labeled toluene, in the reasonable hypothesis that the distribution itself reflects the original sites of the He^3H^+ attack.

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(28) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

(29) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **83**, 4571 (1961).

(30) G. A. Olah, S. J. Kuhn, and B. A. Hardie, *ibid.*, **86**, 1055 (1964).

(31) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962).

(32) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffott, and N. A. Overchuck, *ibid.*, **86**, 1046 (1964).

(33) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

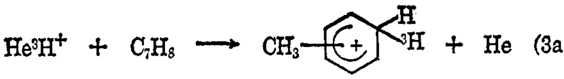
(34) H. C. Brown and B. H. Bolto, *ibid.*, **81**, 3320 (1959).

(35) A. T. Jurewicz, J. H. Bayless, and L. Friedman, *ibid.*, **87**, 5788 (1965).

(36) M. S. B. Munson and F. H. Field, *ibid.*, **89**, 1047 (1967).

(37) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966).

The data of Table III clearly indicate that the He^3H^+ ion attacks preferentially the aromatic ring and, within the ring, the *ortho* and *para* positions. Such findings suggest that the reaction 3 produces a protonated intermediate (or better a mixture of isomeric intermediates) similar to those postulated for the electrophilic substitutions occurring in solution.



(3a)

This evidence, based on the actual analysis of the isomeric tritiated toluenes from reaction 3, supports by analogy the suggestion by Munson and Field[36] as to the nature of the intermediate formed from reaction 5. In fact, while these authors were obviously unable to deduce the structure of their protonated ions from the mass spectral data, they suggested that such ions arise from the proton transfer to the aromatic ring portion of the molecule and postulated for the protonated ion a structure analogous to that observed in the solution chemistry.

The Reaction of He^3H^+ Ions with Deuterated Toluene. The mechanism outlined in the previous section for the formation of tritiated toluene, involving in the first step the selective attack of the ring with the formation of the $C_7H_8{}^3H^+$ ion, followed by the thermoneutral transfer of a proton to an inactive molecule, is complicated by the possibility that a tritium ion instead of a proton is transferred in the latter process. In this case, reaction 4 is replaced by the process

$$C_7H_8{}^3H^+ + C_7H_8 \longrightarrow C_7H_8 + C_7H_8{}^3H^+ \qquad (4a$$

It should be noted that the two $C_7H_8{}^3H^+$ species, which appear in both sides of eq 4a, are not necessarily equivalent. In fact, if the loss of a triton is significant in comparison with the loss of a proton, the labeled $C_7H_8{}^3H^+$ ions (and the labeled toluenes they eventually form) are actually the product of the reactions of two different electrophiles, *i.e.*, the He^3H^+ and $C_7H_8{}^3H^+$ ions, whose substrate and positional selectivity is not necessarily the same. Under such circumstances, it would be obviously arbitrary to deduce the original site of attack by the He^3H^+ ion from the distribution of the tritium within the labeled toluene.

Assuming that the protonated intermediate has the structure given in eq 3a, the competition between processes 4 and 4a, *i.e.*, between the loss of a proton and of a triton, is determined by the relative rates of cleavage of a C–H bond *vs.* a C–^{3}H bond. It can be expected that, owing to the large isotope effect, the loss of protium is here considerably faster. In the hypothesis that, despite the isotope effect, the $^3H^+$ loss is kinetically significant, then the replacement of protium with deuterium in the organic substrate can be expected to enhance considerably the probability of the $^3H^+$ elimination. In fact, the competition between processes 4 and 4a is now determined by the relative rates of cleavage of a C–^{2}H bond *vs.* a C–^{3}H bond, which involves a smaller isotope effect. As a conclusion, the replacement of protium with deuterium in the aromatic substrate can be expected to increase the contribution, if any, of the Brønsted acid $C_7H_8{}^3H^+$ to the formation of the labeled toluene.

The failure to observe any change in the positional (Table III) and the substrate selectivity when the reaction is carried out with deuterated toluene can be explained by two reasons, or by a combination of them: (i) the loss of $^3H^+$ from the charged intermediate is consiherably slower than the loss of $^2H^+$, and, *a fortiori*, than the loss of $^1H^+$; (ii) the differences in the positional and substrate selectivity of the two Brønsted acids, the He^3H^+ and $C_7H_8{}^3H^+$ ions, are not large and cannot be detected in the products analysis. In any event, the experiments carried out with deuterated toluene indicate that the distribution of tritium within the molecule of the labeled toluene is not affected by reaction 4a and therefore can be correctly used to deduce the original sites of attack by the He^3H^+ ion.

Formation of Labeled Methane and Benzene. Besides toluene, only minor amounts of tritiated methane and benzene were identified among the reaction products.

The yield of methane is affected by an unusually high uncertainty for the reasons discussed in a previous section, and therefore the data listed in Table I must be regarded at best as rough approximations. A likely source of tritiated methane appears to be the process

$$He^3H^+ + C_7H_8 \longrightarrow C_6H_5{}^+ + CH_3{}^3H + He \qquad (6)$$

The formation of $C_6H_5{}^+$ ions, through a reaction analogous to process 6, was not observed by Munson and Field in their mass spectrometric study on the protonation of toluene with $CH_5{}^+$ ions.[36] It should be noted, however, that with their protonating agent the reaction is endothermic by 24 kcal/mole, while process 6 is exothermic by *ca.* 50 kcal/mole. Moreover, Munson and Field did actually observe the occurrence of processes analogous to reaction 6, when energetically allowed, as in the protonation of cumene with $CH_5{}^+$ ions.

Among the many processes that can be considered for the formation of tritiated benzene, the attack of the $^3He^3H^+$ ion on the carbon bearing the methyl group seems particularly attractive

$$He^3H^+ + C_7H_8 \longrightarrow C_6H_5{}^3H + CH_3{}^+ + He \qquad (7)$$

Again, the corresponding reaction of the $CH_5{}^+$ ion is endothermic and was not observed,[36] while process 7 is energetically possible. It can be added that the attack of electrophilic reagents on a carbon bearing a methyl group was recently shown[38] to occur at a rate comparable with the rate of attack on a hydrogen-bearing carbon. It cannot be excluded, of course, that at least part of the labeled benzene arises from a different decomposition process of the excited $C_7H_8{}^3H^+$ formed from process 3 and from the consecutive reactions of the labeled fragments.

Conclusions

The essential features of the aromatic electrophilic substitutions occurring in solution are exhibited by the gas-phase reaction of He^3H^+ ions, formed from the β decay of molecular tritium, with toluene. The low

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(38) E. Baciocchi and G. Illuminati, *J. Am. Chem. Soc.*, **89**, 4017 (1967).

substrate and positional selectivity of the He^3H^+ ion, comparable with those observed in the reactions of poorly solvated alkyl ions in aprotic solvents, can be explained on the grounds of the exceedingly high reactivity of the unsolvated, gaseous reagent.

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Stereospecificity in the Chelation of Aspartic Acid

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Abstract: It has been shown that the steric requirements of D- (or L-) aspartate, functioning as a tridentate ligand, dictate the formation of both geometric and optical isomers in the complex [Co(D- or L-aspartate)(diethylenetriamine)]$^+$. Consideration of the relationship between the optical activity (circular dichroism, CD) resulting from the presence of the asymmetric amino acid in the complex and the chirality described by the chelate rings permits a tentative assignment of configuration to the three isomers found. These assignments are in accord with chromatographic behavior and visible absorption data. It has been found that the CD attributable to chelated aspartic acid in these isomers is similar to that observed for aspartic acid in [Co(L-Asp)$(NH_3)_3$]$^+$. The differences, though, raise some interesting questions concerning the source of optical activity in chelate complexes.

The stereochemistry of complexes of a certain class of amino acids and polypeptides containing these amino acids is being investigated. These amino acids (aspartic acid, glutamic acid, cysteine, homocysteine, methionine, etc.) have three donor sites and are consequently potentially tridentate ligands. Although amino acids functioning as bidentates have been extensively investigated,[2] little work on tridentate amino acids has been reported and none with cobalt(III) complexes of these acids. Proton nmr contact shifts[3] and X-ray crystallography[4] were used to establish the tridentate nature of histidine complexes of certain dipositive metal ions, and infrared spectroscopy supported tridentate coordination of aspartic acid in the bisaspartatocopper(II) anion.[5]

These chelated tridentate amino acids are expected to have some interesting stereochemical properties not found for the bidentate amino acids. Consider the geometric and optical isomers of [Co(D-Asp)(dien)]$^+$ (D-Asp = D-aspartate and dien = diethylenetriamine) which might be expected to form (Figure 1) without taking into consideration the steric requirements of D-aspartate. Indeed, with a similar ligand, such as $^-OOCCH_2CH_2NHCH_2COO^-$, all the isomers shown in Figure 1 would be expected, and, for the symmetrical ligand iminodiacetic acid (IDA) in the analogous complex [Co(IDA)(dien)]$^+$, the three expected geometric isomers were found:[6] *trans* (I in Figure 1), s-*cis* (II), and u-*cis* (III and IV identical).

An examination of Hirschfelder molecular models shows that D- (or L-)aspartate can only span a face and furthermore will show absolute stereospecificity on coordination. For the isomer formed from D-aspartate shown in Figure 2, the six- and five-membered rings must be on the left and right, respectively. In the other configuration (six- and five-membered rings reversed), the rings are extremely strained. That is, only one optical isomer of II, III, and IV can form with a given antimere of the amino acid: D-aspartate[7] (Figure 2) should form II-A, III-A, and IV-B; and L-Asp, II-B, III-B, and IV-A. This report is concerned with the preparation, isolation, and study of the circular dichroism (CD) of these isomers and of the related complex [Co(L-Asp)$(NH_3)_3$]$^+$.

Experimental Section

Silver D-Aspartate. Ag_2D-Asp (D- and L-aspartic acid from K & K Laboratories and Aldrich Chemical Co., respectively) was prepared using a method previously described for the preparation of silver salts of aminodicarboxylic acids.[6] The salt was kept shielded from the light to prevent darkening.

s-*cis*-D-Aspartato(diethylenetriamine)cobalt(III) Nitrate. During the following operations, the solution was constantly stirred between 65 and 67°. [$CoCl_3$(dien)],[8] 8.06 g (0.03 mole), was dissolved in 150 ml of water, and 3 g of decolorizing charcoal was added. After 10 min Ag_2D-Asp, 10.4 g (0.03 mole), was added in small portions (5 to 10 min), and the solution was stirred 10–15 min. A solution of 5.30 g (0.0312 mole) of silver nitrate in 30 ml of water was added dropwise (5 min). After 5 min the stirring was stopped, and the solution was allowed to cool for 2 hr. The silver chloride and charcoal were removed by filtration (medium fritted disk), and the solution was evaporated in air to about 20 ml. The red-orange

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[2] See, for example, D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *J. Am. Chem. Soc.*, **89**, 1082 (1967); L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967); R. G. Asperger and C. F. Liu, *ibid.*, **6**, 796 (1967); J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967); M. D. Alexander and D. H. Busch, *ibid.*, **5**, 1590 (1966); R. G. Denning and T. S. Piper, *ibid.*, **5**, 1056 (1966); J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem., Radiochem.*, **9**, 204 (1966), and references therein.

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