Selective Detection of the Tolyl Cation Among Other $[C_7H_7]^+$ Isomers by Ion/Molecule Reaction with Dimethyl Ether

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The ion/molecule reaction of the tolyl cation with dimethyl ether has been investigated using triple quadrupole mass spectrometry. Three isomers with $[C_7H_7]^+$ composition, the 3-tolyl, benzyl, and tropylium cations, were individually selected and reacted with dimethyl ether at a pressure of 1 mtorr in the second quadrupole (Q_2) collision cell. Only the tolyl ion reacted to yield a methoxylated product ion peak at m/z 122. This reaction product having m/z 122 is postulated to be identical in structure with the molecular ion of 3-methyl anisole, as supported by thermochemical data and the similarity of the collision induced dissociation (CID) daughter ion mass spectra of the product ion and the molecular ion of authentic 3-methyl anisole. The daughter ion mass spectra of the three $[C_7H_7]^+$ isomers during CID, by using a triple quadrupole mass spectrometer, are nearly identical; on the other hand, the analytical approach based on the ion/molecule reaction with dimethyl ether clearly exhibits distinct gas-phase chemistry reflecting structural differences among the isomers. (*J Am Soc Mass Spectrom* 1991, 2, 270–277)

Perhaps the most widely investigated ionic isomers in the gas phase are those with $[C_7H_7]^+$ composition [1]. Most of the attention has been directed toward the three isomers shown in Figure 1: the tropylium cation (1), the benzyl cation (2), and the 3-tolyl cation (3). In the effort to distinguish these individual species, high-energy collisional activation (CA) mass spectrometry has been utilized with some success [2–6]. Minor differences in the relative abundances of the fragment ions in the m/z 74– m/z 77 region are observed when the individual ionic species (1), (2), and (3) are generated in the ion source and subjected to high energy CA with a target gas. These variations in relative abundances provide valuable structural information that is used to “fingerprint” the individual ionic species.

Despite the success of CA methodology, disadvantages exist with this technique. The primary disadvantage is that the capacity to distinguish the isomers (1), (2), and (3) is dependent on the reproducibility of specified ratios of daughter ion abundances. The mass-to-charge values of the peaks in the daughter ion mass spectra are identical; there are no unique daughter ion peaks that unequivocally characterize the individual isomers using the high energy CA approach.

An alternative approach for analysis of $[C_7H_7]^+$ ions has been to exploit their unique reactivity with neutral molecules [1]. Ion cyclotron resonance (ICR) mass spectrometers are usually chosen for these ion/molecule reaction studies, although some work has been done utilizing high pressure ion sources. Tropylium ions have been found to be nonreactive in attempts to utilize ion/molecule reactions as structural probes [1]. However, both the benzyl and tolyl ions are reactive with a variety of neutral reagent molecules, thereby permitting these ions to be characterized via an ion/molecule reaction [7–14].

The triple quadrupole mass spectrometer offers a reaction chamber in Q_2 , providing an environment for studying ion/molecule reactions, an approach used previously by other investigators [15–30]. Heretofore, little effort has been directed toward differentiating these $[C_7H_7]^+$ isomers by low energy reactive collisions in a triple quadrupole mass spectrometer (TQMS). Our research has shown that at collision energies up to 100 eV (Lab), the collision-induced dissociation (CID) daughter ion mass spectra of these three isomers are virtually identical. However, by replacing the inert collision gas molecules with reactive molecules, ion/molecule reactions in the collision cell may distinguish the structures of $[C_7H_7]^+$ isomers. In this article, we describe our work utilizing ion/molecule reactions with dimethyl ether (DME) in the center quadrupole reaction chamber of a TQMS for selective detection of the tolyl cation. Of the three isomers (1), (2), and (3), only the tolyl cation (3) reacts

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Figure 1. Structure and heats of formation of three $C_7H_7^+$ isomers. Heats of formation for (1) and (2) were found in ref 32, ΔH_f of (3) is from ref 31.

with dimethyl ether to give an ionic product of m/z 122. Results are shown that support the premise that this product ion has the structure of the methyl anisole molecular ion, and that demonstrate the effectiveness of the low energy ion/molecule reaction methodology for selectively detecting the tolyl cation (3) in mixtures known to contain other $[C_7H_7]^+$ isomers.

Experimental

Instrumentation

All experiments were performed on a Finnigan TSQ-70B (San Jose, CA) triple stage quadrupole mass spectrometer. Following ionization of neutral aromatic compounds by electron impact (EI) or chemical ionization (CI), the "pure" reactant ion of m/z 91 with structure (1), (2), or (3) was selected by the first quadrupole (Q_1) and passed to the collision cell. The neutral reagent gas was introduced into the Q_2 collision cell via the stainless steel gas lines, to indicated pressures of 1×10^{-6} to 8×10^{-6} torr measured by a remote ionization gauge; this corresponds to approximate Q_2 pressures of 0.2 mtorr to 1.5 mtorr, as measured by a Convectron gauge. Following reaction with the neutral vapor, a product ion mass spectrum was obtained by scanning the second mass analyzer, Q_3 . This yielded a mass spectrum, which we call a product ion mass spectrum, indicating the mass-to-charge values for the reaction products formed in the collision cell. The collision energy was 1–2 eV_{lab} (laboratory frame of reference), which optimized the detection of ion/molecule reaction products. For the studies in which the electron energy was varied during the ionization of the neutral precursor, energy values are reported as indicated by the Finnigan TSQ-70B data system.

Generation of "Pure" Isomers

Tropylium cation. "Pure" tropylium ions were generated by either 70-eV EI of the tropylium tetrafluoroborate salt (Aldrich Chemical Co., Milwaukee, WI) [6], introduced into the mass spectrometer ion source via the direct insertion probe, or by EI of toluene at an ion source pressure of ~ 0.1 torr [2].

Benzyl cation. The benzyl cation was generated by low energy EI ionization of benzyl bromide (Aldrich Chemical Co.) [6]. Benzyl bromide was introduced into the ion source via a controlled variable leak valve.

Tolyl cation. Tolyl cations were initially generated by methane CI of 3-fluorotoluene (Aldrich Chemical Co.) [2]. However, later in our investigations, the tolyl cation was generated by low energy EI of 3-nitrotoluene (Aldrich Chemical Co.) [2, 6]. To generate a steady production of the tolyl ion with m/z 91, the precursor neutral molecules were introduced into the ion source via a controlled leak valve.

Gas Chromatography Combined with Tandem Mass Spectrometry Analyses

The Finnigan TSQ-70B instrument was equipped with a Varian (Walnut Creek, CA) 3400 gas chromatograph that was used over the course of this study to introduce a prepared mixture consisting of substituted aromatic compounds known to produce specific isomers or mixtures of isomeric $[C_7H_7]^+$ ions. The mixtures of aromatic compounds (described below) were separated on a DB-5 capillary column (30 m $\times$ 0.25 mm, J & W Scientific, Inc., Rancho Cordova, CA). Helium was used as the carrier gas at a flow rate of 1 mL/min. The column was operated with a splitless injector and, following an injection, the gas chromatograph oven temperature was held at 60 °C for three minutes, ramped to 90 °C at 4 °C/min, and then ramped from 90 °C to 180 °C at 6 °C/min.

All chemicals, including all three isomers of methyl anisole, used throughout this study were purchased from Aldrich Chemical Company (Milwaukee WI), and were used without further purification. The purity of the described test mixture, prepared in our laboratory, was confirmed by gas chromatography-electron impact mass spectrometry.

Results and Discussion

Recently, we described ion/molecule reactions of selected hydrocarbon ions with methanol in the center quadrupole of a TQMS [15]. Only aromatic ions with a vacant site on an aromatic ring carbon reacted with methanol to give a hydroxylation product ion. Additional experiments with other neutral reagents revealed that dimethyl ether reacts in a similar fashion resulting in a methoxylated product ion. The (M-H)⁺ ion of benzene, the phenyl cation, reacts with dimethyl ether to give a methoxylated product ion that suggests a structure such as the molecular ion of anisole. This reaction is 73.1 kJ/mol exothermic. Methoxylation of selected hydrocarbon ions by reaction with DME also requires the cation to contain a

vacant charged site on the aromatic ring. The success of these reactions for detection of aryl cations led us to examine the thermodynamic requirements for selective detection of the tolyl cation among other $[C_7H_7]^+$ isomers, and to test our hypotheses experimentally using this low energy ion/molecule reaction approach in a TQMS.

Thermochemistry

As shown in Figure 1, the tolyl cation is the least stable of the three isomers under investigation [31, 32]. The relatively large heat of formation [31] for the tolyl cation contributes to the greater bond strength for $[C_7H_7^+-X]$ for a variety of ring substituents (Table 1). Conversely, there is more energy generated in formation of a bond with a ring carbon (as with (3)) than with the methylene carbon attached to a benzene ring (i.e., (2)). This thermochemical information aids in our search for a neutral candidate that may selectively react with the tolyl cation. If the energy released in the formation of the $(C_7H_7^+-X)$ bond is greater than the $(R-X)$ bond strength $[D(R-X)]$ for the neutral reactant, the ion/molecule reaction is exothermic. Therefore, a neutral reagent is sought for which the $(R-X)$ bond strength is greater than $D((1)-X)$ or $D((2)-X)$, yet less than $D((3)-X)$. Satisfying these criteria would yield a thermodynamically favorable ion/molecule reaction for the selective detection of the tolyl cation. It has been our experience in investigating ion/molecule reactions in Q_2 that ionic products formed by ion/molecule reactions are observed only for thermoneutral or for exothermic reactions. In considering neutral reagent candidates, methyl iodide, for example, would not be expected to react with any

of the $[C_7H_7]^+$ isomers to form $C_7H_7I^+$ because the reaction would be endothermic in all cases; the (CH_3-I) bond strength is greater than the $D(C_7H_7^+-I)$ for the benzyl and tolyl isomers. Upon examination of Table 1, a few neutral species emerge as reactant candidates that would be selective for (3); these include methanol, dimethyl ether, and ammonia.

Experimental Results

To test our hypothesis that the tolyl cation will react selectively with methanol or dimethyl ether, the individual "pure" isomers of (1), (2), or (3) were generated in the ion source, as indicated in the Experimental section, and the ions with m/z 91 were chosen for reaction with the reagent in the collision cell. A product ion mass spectrum for each individual isomer upon reaction with methanol was obtained (data not shown), and only the tolyl cation gave a product ion peak, which was detected at m/z 108, representing the addition of $\cdot OH$. This same protocol was performed with dimethyl ether as the reagent gas, and the product ion mass spectrum, corresponding to the reaction of the 3-tolyl cation with DME at a pressure of 1 mtorr, is shown in Figure 2. The dominant ion/molecule reaction product ion is represented by a peak at m/z 122. Minor peaks are observed at m/z 45 representing the $(M-H)^+$ ion of dimethyl ether formed by hydride abstraction, and at m/z 65 representing a CID fragment ion (loss of C_2H_2) from the tolyl cation. There are no product ion peaks observed when the benzyl cation or tropylium cation, generated from the appropriate neutral precursor, is individually selected and reacted with DME at the same collision conditions. These results are consistent with predictions

Table 1. Bond strengths in kJ/mol^a

	$D(C_7H_7^+-X)$ in kJ/mol			Neutral molecule
	$D((1)-X)$	$D((2)-X)$	$D((3)-X)$	$(R-X)$	$D(R-X)$
X = H	85	204	371	R = CH ₃	438
	"	"	"	R = C ₆ H ₅ CH ₂	372
X = OH	—	216	425	R = CH ₃	386
X = Cl	—	121	305	R = CH ₃	349
X = CH ₃	—	168	357	R = CH ₃	376
X = OCH ₃	—	132	402	R = CH ₃	345
X = NH ₂	—	168	465	R = CH ₃	358
	—	"	"	R = H	453
X = I	—	71	196	R = CH ₃	237
X = CN	—	245	405	R = CH ₃	507
X = CHCH ₂	—	176	418	R = H	431
X = COCH ₃	—	132	296	R = H	360

^a Bond strengths calculated from neutral and ionic heats of formation found in refs 31 and 32.

Figure 2. Product ion mass spectrum of 3-tolyl cation with dimethyl ether in the collision cell at an indicated pressure of 4.4×10^{-6} torr, which corresponds to ~ 1 mtorr in Q_2 . The collision energy was 2 eV_{Lab}.

from the thermochemistry and suggest that either methanol or dimethyl ether may be used as a reagent gas for selective detection of the tolyl cation. In our studies of the ion/molecule reactions of $[C_7H_7]^+$ isomers, DME is the preferred reagent gas, primarily due to the ease with which DME is introduced (DME is a gas at standard temperature and pressure) into the mass spectrometer.

We postulate that the product ion having m/z 122 formed by the reaction of the 3-tolyl cation and DME represents an ion structure identical to that of the molecular ion of 3-methyl anisole (4), as suggested in Scheme 1. This reaction is 57 kJ/mol exothermic. Product ions formed by low energy collisions of the reactant ion with a neutral reagent in the center quadrupole may be detected only if the reaction is exothermic or thermoneutral, and if there is sufficient reaction time. In contrast to the favorable thermochemical conditions for the methoxylation reaction of the tolyl cation with DME, the reaction enthalpy of the benzyl cation with DME to form a methoxylated product ion is +213 kJ/mol, whereas reaction with tropylium would be expected to be more endothermic, due to the even higher stability of the tropylium cation.

Evidence for the structure of the reaction product ion of m/z 122 was obtained by comparing the CID daughter ion mass spectrum of the product ion with that of the molecular ion of 3-methyl anisole (4). (At the suggestion of a referee, we also obtained the CID

Figure 3. (a) The collision-induced dissociation (CID) daughter ion mass spectrum of the reaction product of m/z 122 formed in the ion source when 3-nitrotoluene and dimethyl ether were introduced simultaneously. (b) The CID daughter ion mass spectrum of the molecular ion of authentic 3-methyl anisole. The collision conditions were identical for both experiments; argon pressure in the collision cell was 0.2 mtorr and the collision energy was 25 eV_{Lab}.

mass spectra of 2- and 4-isomers of methyl anisole; these are similar in that the ratio of daughter ion peaks at m/z 92 and m/z 107 is approximately 0.2. In contrast, the CID mass spectrum of 3-methyl anisole reproducibly shows the daughter ion peaks at m/z 92 and m/z 107 in a ratio of approximately 1.2, as illustrated in Figure 3b.) The reaction product ion of m/z 122 was formed when dimethyl ether was introduced simultaneously with 3-nitrotoluene into the ion source. Under low energy EI conditions, the initially formed tolyl ion reacts with DME in the source to give the product ion of m/z 122, which is then subjected to CID. The CID daughter ion mass spectrum of m/z 122 is shown in Figure 3a. Figure 3b is the CID daughter ion mass spectrum of the molecular ion of

$$\Delta H_{\text{rxn}} = -57 \text{ kJ/mol}$$

Scheme 1

authentic 3-methyl anisole. Although there is some difference in the relative strength of these daughter ion mass spectra (probably a threefold greater attenuation of the parent ion in Figure 3a due to a slightly higher Ar pressure), the similarity of these two daughter ion mass spectra provides additional evidence for the structure of the product ion as suggested by Scheme I.

Having established under ion/molecule reaction conditions for these three $[C_7H_7]^+$ isomers with DME that only the tolyl cation formed a detectable product ion, the utility of this reaction was evaluated. A simple mixture was prepared with components listed in Table 2. Each component was present at an approximate concentration of 20 ng/ μ L. One microliter of the mixture was injected into the gas chromatograph and, following ionization by 70-eV electrons, the ion current at m/z 91 was selected and passed to Q_2 , which contained DME at an indicated ion gauge pressure of 1×10^{-5} torr. If any of the ions of m/z 91 had the tolyl structure, then a peak at m/z 122 was anticipated in the product ion mass spectrum. The results of this experiment are shown in Figure 4, which is a composite of the reconstructed mass chromatograms at m/z 91 (4a) and at m/z 122 (4b). Coincidence of peaks in the two mass chromatograms for h, i, and j suggest that, at the least, some of those ions with m/z 91 have the tolyl structure (3); this observation is in agreement with recently published results as summarized in Table 2 [6]. Our results indicate that none of the other components in this test mixture generate tolyl cations under the stated ionization conditions.

It is interesting to compare the low energy CID daughter ion mass spectra of m/z 91 representing two predominantly different ionic structures. Figure 5 shows the CID daughter ion mass spectra of the ion of m/z 91 from 2-bromotoluene (Figure 5a) and 3-

Table 2. Components in test mixture to be separated by gas chromatography

	% Tolyl @ 70-eV EI ^a (CA results)
(a) o-Chlorotoluene	3
(b) m-Chlorotoluene	24
(c) p-Chlorotoluene	3
(d) Benzyl methyl ether	NR
(e) o-Bromotoluene	3
(f) p-Bromotoluene	3
(g) Benzyl bromide	NR
(h) m-Iodotoluene	40
(i) m-Nitrotoluene	57
(j) p-Nitrotoluene	70

^aResults taken from ref 6. CA, collisional activation; NR, not reported.

nitrotoluene (Figure 5b), respectively. The CID daughter ion mass spectra of these two isomeric ions appear nearly identical at a collision energy of 25 eV_{Lab}, yet the difference in reactivity of these two ions with DME, as shown in Figure 4, is great and can be used to distinguish the ionic structures. The ions of m/z 91 were produced under identical conditions for the experiments represented in Figures 4 and 5.

Another assessment of the selectivity and quantitative nature of the ion/molecule reaction was conducted under conditions that isomerize $[C_7H_7]^+$ in a known manner [6]. It is known that during dissociative ionization of 3-nitrotoluene, "pure" tolyl ions are generated at low electron energy [6]. As the electron energy is increased, isomerization to the more stable benzyl structure occurs in the ion source, prior to sampling in the collision cell. With the ion/molecule analytical approach, at the very least, a relative assessment of the tolyl composition present in $[C_7H_7]^+$

Figure 4. Reconstructed mass chromatograms of (a) m/z 91 and (b) m/z 122 when a mixture of components identified in Table 2 was injected into the gas chromatograph and the ion of m/z 91 was chosen to react with dimethyl ether in the second quadrupole at a pressure of 1 mtorr and collision energy of 2 eV_{Lab}.

Figure 5. Collision-induced dissociation daughter ion mass spectrum of m/z 91 generated by 70-eV electron impact of (a) 2-bromotoluene and (b) 3-nitrotoluene. Collision energy was 25 eV_{Lab} and argon was the collision gas at a pressure of 0.3 mtorr. The peaks at m/z 91 are off-scale by a factor of approximately twentyfold.

mixtures can be established. The ratio of $I_{122}/(I_{122} + I_{91})$ should reflect the relative tolyl composition of $[C_7H_7]^+$ mixtures (where I_{122} and I_{91} represent the ion current at m/z 122 and m/z 92, respectively). The relative composition of the $[C_7H_7]^+$ mixture from 3-nitrotoluene, as a function of electron energy, was investigated by measuring the $I_{122}/(I_{122} + I_{91})$ ratio for three different pressures of DME, and the results are depicted in Figure 6. Each data point represents the results of 40–50 averaged scans. The tolyl ion content, reflected by the $I_{122}/(I_{122} + I_{91})$ ratio, decreases as the electron energy is increased from 12 eV to 20 eV; after 20 eV, the tolyl ion content remains relatively constant. These results suggest, as expected, that the relative amount of tolyl cations in

Figure 6. Ratio of $I_{122}/(I_{122} + I_{91})$ from Q_3 as a function of electron energy (in the ion source) during electron impact of 3-nitrotoluene and transmission of ion current at m/z 91 into Q_2 for reaction with dimethyl ether at the indicated pressures.

Table 3. Enthalpies of reactions leading to the formation of $C_8H_9^+$ and methanol^a

	ΔH_{rxn} (kJ/mol)
(1) + $CH_3OCH_3 \rightarrow (C_7H_6)CH_3^+ + CH_3OH$	-7.6
(2) + $CH_3OCH_3 \rightarrow C_6H_5C^+HCH_3 + CH_3OH$	-83.6
(3) + $CH_3OCH_3 \rightarrow 3-C_6H_4(CH_3)CH_2^+ + CH_3OH$	-217

^aHeats of formation found in refs 32 and 34.

$[C_7H_7]^+$ mixtures generated by EI of 3-nitrotoluene is greater at low electron energy than at high electron energy.

Effect of Higher Gas Pressure

As alluded to above, the enthalpy of the reaction is not the only factor that determines whether product ions are formed in the second quadrupole with subsequent detection as peaks in the product ion mass spectrum. The ion/molecule reaction kinetics also must be considered. The absence of a peak at m/z 105 in the product ion mass spectra of the $[C_7H_7]^+$ cations with DME is noteworthy. The ion/molecule reaction of the tolyl cation with DME, to yield a methylbenzyl cation at m/z 105 and neutral methanol, is more favored thermodynamically than is the reaction yielding the methoxylation product ion and a methyl radical; the ΔH_{rxn} s are -217 kJ/mol and -57 kJ/mol, respectively [32]. However, this peak at m/z 105 is very minor in the product ion mass spectrum. The thermochemistry also reveals, as shown in Table 3, that reactions of benzyl and tropylium cations to form $[C_8H_9]^+$ ions are favorable, yet product ions with m/z 105 are not detected at a Q_2 pressure of 1 mtorr DME. If, however, the pressure of DME is raised to 3 mtorr, the product ion mass spectra derived from all three isomers give rise to peaks at m/z 105 and m/z 137, as shown in Figure 7. The product ion peak at m/z 122 is still unique to the tolyl cation. In all three cases, the product ion of m/z 137 represents the intermediate collision complex, $(C_7H_7 \cdots DME)^+$, which is stabilized at higher gas pressures by third-body collisions within Q_2 . The peak at m/z 105 represents the ion with $[C_8H_9]^+$ composition, with suggested structures shown in Table 3. Higher reagent gas pressure is required, so it follows that, kinetically, the reaction to form the $[C_8H_9]^+$ cation of m/z 105 proceeds slower than the ion/molecule reaction of the tolyl cation and DME, which produces the ion of m/z 122, proposed to be the molecular ion of methyl anisole. Raising the collision pressure increases the lifetime of the collision complex of m/z 137, as is evident by the detection of ion current at m/z 137, allowing access to slower reaction channels. Hydrogen rearrangement is necessary in the sequence forming $[C_8H_9]^+$ ions and neutral methanol; this is a slower reaction than the tolyl-DME methoxylation reaction (Scheme I), where only simple bond formation and cleavage is necessary to form the products.

Figure 7. Product ion mass spectrum of (a) tolyl cation, (b) benzyl cation, and (c) 3-tropylium cation in reaction with dimethyl ether in Q_2 at a pressure of ~ 3 mtorr. The collision energy was 1 eV_{Lab}.

Reaction with Ammonia

It was demonstrated previously that reaction of the phenyl cation with ammonia produces a product ion of m/z 93, which is identical in structure to the molecular ion of aniline [33]. The bond energies shown in Table 1 suggest that the addition of NH_2 may occur in the reaction of the tolyl cation with NH_3 , whereas it is not anticipated in reaction with the benzyl or tropylium cations. Once again, the individual isomers were generated in the ion source and reacted with ammonia at a pressure of 1 mtorr (data not shown). No product ion peaks were detected during the reaction of NH_3 with (1) or (2), but for (3), a peak was detected at m/z 93, not as expected at m/z 107. Consideration of the thermodynamics of the reaction provides insight into the chemistry that is occurring; the reaction enthalpy to form the methyl substituted aniline molecular ion is 12 kJ/mol exothermic, whereas the enthalpy of the reaction forming the ion of m/z 93, presumably representing the molecular ion of aniline, is -33 kJ/mol [32].

Conclusion

A novel approach for selective detection of the tolyl cation among other $[\text{C}_7\text{H}_7]^+$ ions has been developed based on its unique reactivity with DME. The results suggest that the methoxylated product ion of m/z 122 is identical in structure to the molecular ion of methyl anisole; this suggestion is based on thermochemical calculations and comparison of CID daughter ion mass

spectra. The results recommend the use of triple quadrupole mass spectrometry for detection and quantification of the tolyl cation in isomeric $[\text{C}_7\text{H}_7]^+$ mixtures. Our search continues for an ion/molecule reaction (utilizing a TQMS) that would be selective for the benzyl cation or the tropylium cation. For an ion/molecule reaction to be thermodynamically favorable for either the benzyl or tropylium cations, but not the tolyl cation, the relative stability of the reaction products formed in the ion/molecule reaction must overcome the differences in the ΔH_f between the $[\text{C}_7\text{H}_7]^+$ reactant cations (Figure 1). If these reactions can be accomplished in the center quadrupole of a TQMS, then perhaps complete quantification of $[\text{C}_7\text{H}_7]^+$ mixtures could be made by this low energy ion/molecule reaction approach.

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