Aromatic Substitution in the Gas Phase. Alkylation of Arenes by $C_4H_9^+$ Ions from the Protonation of C_4 Alkenes and Cycloalkanes with Gaseous Brønsted Acids

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Use of a reactive aromatic substrate (*o*-xylene) to sample the isomeric population of the butyl ions from the gas-phase protonation of the C_4H_8 hydrocarbons shows that the primary product from linear olefins and methylcyclopropane is the s-butyl ion, or at least an s-butylating charged species displaying a positional selectivity very similar to that measured for the thermal s-butyl cations obtained from n-butane. A fraction of the primary $C_4H_9^+$ ions isomerizes to the most stable tertiary structure, to an extent which depends, *inter alia*, on the exothermicity of the proton transfer process. Protonation of cyclobutane gives an alkylating reagent whose s-butylation/t-butylation ratio and positional selectivity set it apart from the $C_4H_9^+$ reagents obtained from the other C_4H_8 hydrocarbons, suggesting the intervention of a different electrophile, conceivably protonated cyclobutane. Finally, protonation of isobutene yields exclusively a t-butyl ion that does not isomerize despite the large exothermicity of its formation.

DESPITE the impressive literature on Friedel–Crafts aromatic alkylation,[1] considerable uncertainties attach to general aspects of its mechanism, firmly established only in a relatively few cases.[2,3] This arises, in part, from the complicating effects of the many different components of the reaction medium, *i.e.* the reagents, solvents, catalysts, promoters, *etc.* used in countless combinations for the study of any given Friedel–Crafts alkylation

Since the gas phase represents the simplest reaction environment, free in particular from the complicating effects of solvation and counterions, the study of aromatic substitution by gaseous carbenium ions is particularly attractive, in that it may eventually provide a simplified model, capable of accomodating in a general and economical way the staggering variety of data from solution chemistry experiments.

To this end, gas-phase alkylation of selected aromatic substrates with simple carbenium ions has been previously investigated.[3-9] In particular, the reaction of arenes with $C_4H_9^+$ ion from n-C_4H_{10} has been shown to yield exclusively s-butylarenes, remarkably free of isomeric byproducts, in particular of n-, iso-, and t-butylarenes.[10]

This paper reports an extension of the study to the gaseous $C_4H_9^+$ reagent(s) obtained from the protonation of C_4H_8 isomers according to a general procedure widely employed in solution chemistry. The hydrocarbons investigated include but-1-ene, *cis*- and *trans*-but-2-ene, isobutene, cyclobutane, and methylcyclopropane, whose protonation has been carried out with X_3^+ (X = H,D) and $C_nH_5^+$ (n = 1,2) gaseous ions.

o-Xylene has been employed as the aromatic substrate in most experiments owing to its adequate reactivity toward gaseous carbenium ions, including t-$C_4H_9^+$, which has been demonstrated by previous studies. Furthermore, t-butylation of *o*-xylene yields only one product,[10] which considerably simplifies the analytical problem.

EXPERIMENTAL

Materials.—H_2, D_2, CH_4, and O_2 were obtained from Matheson Gas Products Inc., and their stated purity exceeded 99.99 mol%. The butanes and butenes were purchased from the same source, and had a stated purity in excess of 99.9%. Methylcyclopropane was obtained from IGN Pharmaceuticals Inc., while cyclobutane was prepared from cyclobutanone (Fluka AG) according to standard procedures. The purity of all C_4 hydrocarbons, and the absence of unwanted impurities, were checked by g.l.c. on the following columns: (i) 20 ft packed with 10% EDO-1 on 100—120 mesh Chromosorb PAW, operated at 0 °C, and (ii) 2 m packed with 80—100 mesh Carbopack C, modified with 0.9% w/w picric acid, operated at 50 °C.

The aromatic substrates were g.l.c. standards from C. Erba Co.; s- and t-butylarenes, used as reference standards, were obtained from Aldrich Chemical Co., or prepared according to standard procedures, their identity being established by n.m.r. and i.r. spectroscopy.

Procedure.—The gaseous samples, prepared as previously described,[10] were irradiated in a 220 Gammacell (Nuclear Canada Ltd.) to a total dose of 2—4 Mrad, at the rate of 0.5 Mrad h^{-1}, at 30 °C. The products were analysed by g.l.c. using a Sigma 1 chromatograph (Perkin-Elmer Co.) equipped with an f.i.d. unit, on the following columns: (i) 6 ft packed with 80—100 mesh Carbopack C, modified with 0.1% w/w SP-1000, at temperatures up to 205 °C, (ii) 6 ft packed with 5% SP-1200 + 1.75% Bentone 34 on 100—120 mesh Supelcoport, at 100 °C, and (iii) a 150 ft Carbowax C 20M capillary column, operated at 95 °C. Individual calibration factors were used for the quantitative analysis of the products, whose identity was confirmed using a model 5982 A Hewlett-Packard mass spectrometer, having the Carbowax C 20M capillary column directly inserted into the ion source. The mass spectral data were recorded and processed with a model 5934 A data system from Hewlett-Packard.

RESULTS

Absolute Yields.—Butylarenes are formed in all irradiated systems, and the ionic character of alkylation is concurrently demonstrated by the strong inhibiting action of NH_3, an effective interceptor of all isomeric $C_4H_9^+$ cations,[11] and by the insensitivity of the yields to the presence of O_2, an effective radical scavenger.

The absolute yield of a given product is expressed by its $G_{(+M)}$ value, calculated from the total amount formed and the radiation dose absorbed by the gas. It must be clearly stated that, owing to the many sources of uncertainties, from dosimetric problems to the unknown effects of accumulating radiolytic products, the experimental G values must be regarded as a rough approximation, affected by errors estimated at *ca.* ±30%.

Nevertheless, consideration of the absolute yields is useful, since their experimental errors do not obscure the large differences among systems containing different C_4H_8 hydrocarbons, nor the systematic decrease of the G values at increasing $[C_4H_8]:[\text{Arene}]$ ratios, clearly apparent from the Figure.

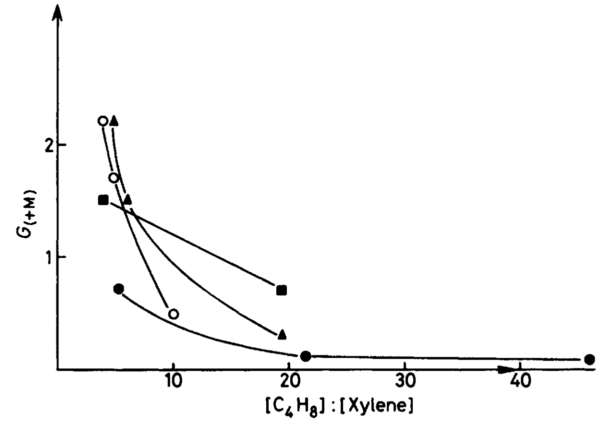


FIGURE Absolute overall yields of butylated aromatics as a function of the $[C_4H_8]:[\text{Arene}]$ ratio in mixtures of H_2, C_4H_8, and *o*-xylene: ●, but-1-ene; ○, *trans*-but-2-ene; ▲, *cis*-but-2-ene; ■, methylcyclopropane

Relative Yields and Isomeric Composition of Products.—These data can be measured with a far better accuracy than the absolute yields. Table 1 gives the composition of the irradiated systems, the relative yields of the products, and their isomeric composition, together with the pertinent data concerning the alkylation with $C_4H_9^+$ ions from n-butane,[10] which are included for comparison purposes. The major features of the results can be itemized as follows.

(i) Protonation of isobutene with X_3^+ and $C_nH_5^+$ yields an alkylating agent that promotes exclusively t-butylation.

(ii) The reagent(s) from the protonation of other C_4H_8 hydrocarbons with X_3^+ promote s- and t-butylation, whose relative extent changes with the $[C_4H_8]:[\text{Arene}]$ ratio.

t-Butylation is appreciably more significant from cyclobutane, methylcyclopropane, and but-1-ene than from but-2-enes.

(iii) The relative extent of s- and t-butylation from a given C_4H_8 hydrocarbon depends on the nature of the protonating reagent, as well as on the exothermicity of the proton transfer process. Thus, the proportion of t-butylated isomer from but-1-ene and *trans*-but-2-ene is much *lower* when the protonation is carried out with the milder $C_nH_5^+$ ions than with the H_3^+ ions.

(iv) Essentially only one isomer is formed in the t-butylation of toluene and *o*-xylene. s-Butylation of *o*-xylene yields both 1,2-dimethyl-3-s-butyl- and 1,2-dimethyl-4-s-butyl-benzene, whose proportions are affected to some extent by the $[C_4H_8]:[\text{Arene}]$ ratio. At a fixed value of the latter, the isomeric composition of the products is approximately the same from all C_4H_8 hydrocarbons, when protonated with X_3^+ ions. Protonation of but-1-ene and *trans*-but-2-ene with $C_nH_5^+$ ions gives an appreciably higher proportion of 1,2-dimethyl-3-s-butylbenzene than protonation with X_3^+ ions under otherwise comparable conditions.

DISCUSSION

The Alkylating Reagent.—Protonation of C_4H_8 hydrocarbons in a gaseous system containing traces of arenes promotes a complex sequence of reactions, eventually leading to the formation of butylated arenes according to processes which are partially illustrated in the Scheme.

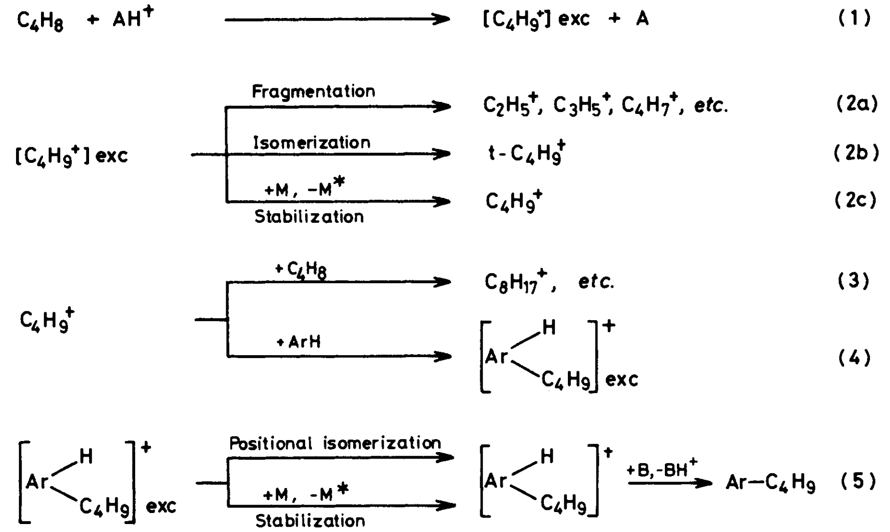
Butyl ions are produced from the protonation of the C_4H_8 hydrocarbons with X_3^+ and $C_nH_5^+$ ions, respectively

TABLE 1

Gas-phase alkylation of arenes with $C_4H_9^+$ ions from the protonation of C_4H_8 hydrocarbons

System composition [a] (Torr)			Relative yields [b] (%)		Isomeric composition of s-butylarenes (%)	
Bulk gas	C_4H_8 Hydrocarbon	Arene	t-Butyl-arenes [c]	s-Butyl-arenes		
H_2 (715)	Isobutene (5.0)	*o*-Xylene (0.65)	98	2		
CH_4 (707)	Isobutene (4.9)	Toluene (0.82)	100			
H_2 (709)	But-1-ene (3.0)	*o*-Xylene (0.58)	31	69	1,2,*3* [d] : 44	1,2,*4* : 56
H_2 (720)	But-1-ene (13)	*o*-Xylene (0.60)	59	41	41	59
H_2 (725)	But-1-ene (28)	*o*-Xylene (0.61)	52	48	43	57
CH_4 (720)	But-1-ene (16)	*o*-Xylene (0.61)	7	93	56	44
H_2 (692)	*cis*-But-2-ene (3.0)	*o*-Xylene (0.73)	14	86	45	55
H_2 (692)	*cis*-But-2-ene (18)	*o*-Xylene (0.93)	47	53	43	57
H_2 (720)	*trans*-But-2-ene (3.0)	*o*-Xylene (0.71)	15	85	48	52
H_2 (720)	*trans*-But-2-ene (3.0)	*o*-Xylene (0.79)	16	84	54	46
H_2 (707)	*trans*-But-2-ene (10)	*o*-Xylene (0.91)	50	50	45	55
CH_4 (720)	*trans*-But-2-ene (15)	*o*-Xylene (0.68)	6	94	57	43
H_2 (720)	Methylcyclopropane (3.0)	*o*-Xylene (0.71)	32	68	44	56
H_2 (695)	Methylcyclopropane (15)	*o*-Xylene (0.78)	72	28	38	62
H_2 (706)	Cyclobutane (8.5)	*o*-Xylene (0.48)	82	18	36	64
n-C_4H_{10} (720)		*o*-Xylene (0.82)	2.7 [e]	97	44	56
n-C_4H_{10} (720)		Toluene (2.7)		100 [e]	*o*- : 42	*m*- : 30 *p*- : 28

[a] All systems contained 3—10 Torr O_2. [b] Standard deviation *ca.* 10%. [c] Only *p*-t-butyltoluene is formed from toluene, only 1,2-dimethyl-4-t-butylbenzene from *o*-xylene. [d] Position of s-butyl group italicized. [e] From ref. 7.



SCHEME Reactions promoted by the protonation of C_4H_8 hydrocarbons in the presence of aromatic substrates

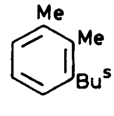
formed from the radiolysis of X_2 and CH_4 bulk gas *via* well established processes.[12,13] The butyl ions are generated in a considerably excited state, owing to the exothermicity of the formation process (1), listed in Table 2. It should be noted that the $C_nH_5^+$ reagents are considerably milder than X_3^+, their attack on C_4H_8 hydrocarbons being less exothermic by 113 (CH_5^+) and 251 ($C_2H_5^+$) kJ mol^{-1} The excited products from (1) can decompose, isomerize, or undergo collisional deactivation, according to competitive processes (2a—c), whose relative extent depends on the excitation level of the $C_4H_9^+$ ions, the pressure, and the nature of the bath gas.

n-$C_4H_9^+$ (I)

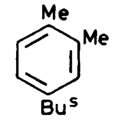
iso-$C_4H_9^+$ (II)

s-$C_4H_9^+$ (III)

t-$C_4H_9^+$ (IV)



(V)



(VI)

Processes (1) and (2) have been directly demonstrated by high-pressure mass spectrometry. Fragmentation plays a significant role when H_3^+ is used as the protonating agent in H_2 gas up to 1 Torr, giving higher abundances of $C_2H_5^+$, $C_3H_5^+$, and $C_4H_7^+$ fragments. At this pressure, only *ca.* 10—15% of the excited butyl ions from but-1-ene, *trans*-but-2-ene, and isobutene are collisionally stabilized.[20] The chemical ionization spectrum of isobutene in CH_4 at 2 Torr is characterized by a much higher (up to 70%) abundance of stabilized $C_4H_9^+$ ions,[21] owing to the lower exothermicity of the proton transfer from $C_nH_5^+$.

At the much higher pressures prevailing in the present investigation, it is reasonable to assume that fragmentation processes (2a) are largely suppressed, as suggested by the lack of aromatic products that can be traced to alkylation by fragment ions, such as $C_2H_5^+$ and $C_3H_5^+$.

TABLE 2

Energetics of the reactions of C_4H_8 hydrocarbons with AH^+ Brønsted acids to yield s-$C_4H_9^+$ and t-$C_4H_9^+$ cations

		$-\Delta H°$/kJ mol^{-1} [a]	
Hydrocarbon	AH^+	s-$C_4H_9^+$	t-$C_4H_9^+$
But-1-ene	H_3^+	369	430
	CH_5^+	256	317
	$C_2H_5^+$	118	179
cis-But-2-ene	H_3^+	362	423
	CH_5^+	249	310
	$C_2H_5^+$	111	172
trans-But-2-ene	H_3^+	358	419
	CH_5^+	245	306
	$C_2H_5^+$	107	168
Isobutene	H_3^+	352	413
	CH_5^+	239	300
	$C_2H_5^+$	101	162
Methylcyclopropane	H_3^+	396	457
	CH_5^+	283	344
	$C_2H_5^+$	145	206
Cyclobutane	H_3^+	396	457
	CH_5^+	283	344
	$C_2H_5^+$	145	206

[a] Calculated from the data of refs. 14—19.

In conclusion, in our systems at atmospheric pressure the alkylating reagent is likely to consist of one of the isomeric butyl ions, *i.e.* n-butyl (I), $H_f°$ 841 kJ mol^{-1}, isobutyl (II), $H_f°$ 833 kJ mol^{-1}, s-butyl (III), $H_f°$ 739 kJ mol^{-1}, and t-butyl (IV), $H_f°$ 678 kJ mol^{-1},[15,22] or their mixtures.

Competition of C_4H_8 *Hydrocarbons and Arenes for the* $C_4H_9^+$ *Reagents.*—The C_4H_9 ions from (1) can react either with the parent C_4 hydrocarbon or with the arene. A rough estimate of the relative reactivity of the two nucleophiles can be deduced from the absolute yields of alkylated aromatics and the known $[C_4H_8]:[Arene]$ ratio, in the admittedly oversimplified assumption that

$C_4H_9^+$ ions react exclusively as an alkylating agent with the aromatic substrate [equation (4)]. Indeed, alkylation is but one of the energetically allowed reaction channels, in that proton transfer (6) and hydride-ion abstraction (7) are exothermic processes as well.[15,23,24]

$$\text{s-}C_4H_9^+ + C_6H_4(CH_3)_2 \longrightarrow C_4H_8 + C_6H_5(CH_3)_2^+ \quad (6)$$

$$\text{s-}C_4H_9^+ + C_6H_4(CH_3)_2 \longrightarrow C_4H_{10} + CH_3C_6H_4CH_2^+ \quad (7)$$

However, previous radiolytic and chemical ionization evidence * suggests that in gaseous systems at atmospheric pressure processes (6) and (7) are comparatively less efficient than (4), and their role can be neglected at the approximation level of the present considerations.

The overall reactivity order of the C_4H_8 hydrocarbons toward $C_4H_9^+$ ions, *i.e.* but-1-ene > *cis*-but-2-ene > *trans*-but-2-ene > isobutene > methylcycopropane > cyclobutane, agrees qualitatively with that expected from the limited mass spectrometric data currently available.[25,26]

It should be noted that consideration of the absolute overall yields of butylated products leads to reactivity ratios that represent weighted averages of the individual reactivity of (III) and (IV) toward a given C_4H_8 isomer. The nature of the experiments does not in fact allow a quantitative treatment of the individual reactivity of (III) and (IV).

Positional Selectivity.—t-Butylation of *o*-xylene gives one isomer, providing further evidence for the inhibiting steric effect of a methyl group toward *ortho*-substitution by the bulky t-$C_4H_9^+$ cation, even in the dilute gas state and lacking any counterion and solvation shell.[7]

s-Butylation of *o*-xylene gives both 1,2-dimethyl-3-s-butylbenzene (V) and 1,2-dimethyl-4-s-butylbenzene (VI) in comparable amounts. The relative proportions of (V) and (VI) from the linear C_4 olefins, protonated with X_3^+ ions, tend to group at *ca.* 45 ± 4 and 55 ± 5%, respectively, which correspond to the 44 : 56 ratio obtained from the alkylation of *o*-xylene with the s-butyl ions from n-butane.[10]

There is no appreciable influence of the nature of the individual linear olefins on the positional selectivity of the alkylation. This supports the view that a common ionic reagent, (III), is obtained from their protonation.

The isomeric composition of products is somewhat different from methylcyclopropane and significantly so from cyclobutane, which yields the highest proportion (64%) of (VI), together with the highest (>80%) extent of t-butylation. These features set cyclobutane apart from the other C_4H_8 isomers and point to the intervention of a different alkylating reagent, possibly protonated cyclobutane, whose occurrence in the gas state has been previously reported.[27] The alternative reaction sequence (8) could explain the predominant t-butylation

$$AH^+ + \text{cyclo-}C_4H_8 \xrightarrow{-A} [\text{c-}C_4H_9^+]_{\text{exc}} \longrightarrow \text{t-}C_4H_9^+ \xrightarrow{+ArH} \text{Products} \quad (8)$$

promoted by protonated cyclobutane. However, process (8) appears unlikely, in the light of previous results showing that cyclo-$C_4H_9^+$ tends to isomerize to (III) rather than to (IV).[28]

s-Butylation versus *t-Butylation.*—According to the Scheme, the relative extent of s- and t-butylation depends on the following factors: (i) the isomeric composition of the primary ions from the protonation step (1); (ii) the extent of the secondary processes (2a) and (2b). (iii) the relative reactivity of (III) and (IV) toward their parent hydrocarbons, which in turn determines the k_3/k_4 ratio, since (III) and (IV) are known [10] to react with *o*-xylene at comparable rates.

The effect of factor (i) can be clearly discerned only in the case of isobutene, whose protonation yields exclusively a t-butylating reagent. This shows, in agreement with recent i.c.r. results,[15] that (IV), the primary product from the protonation of isobutene, does not appreciably isomerize to (III), despite the fact that the exothermicity of (1) largely exceeds the stability difference between (III) and (IV).

All other C_4 hydrocarbons give both s- and t-butylated products, whose proportions depend on the nature of the C_4 hydrocarbon, the exothermicity of its protonation, and the $[C_4H_8]$: [Arene] ratio.

As far as linear olefins and methylcyclopropane are concerned, their protonation yields predominantly (III), or at least a charged moiety that behaves as an s-butylating reagent. Thus s-butylarenes account for over 90% of the alkylation products when the relatively mild $C_nH_5^+$ ions are used as the protonating agent.

The operation of factor (ii) can be inferred from the larger extent of t-butylation promoted by the X_3^+ ions with respect to $C_nH_5^+$, following protonation of any linear olefin, *e.g.* but-1-ene. The higher exothermicity of the proton transfer from X_3^+ leads to formation of more highly excited $C_4H_9^+$ ions, which undergo a correspondingly faster skeletal isomerization. Rearrangement of excited (III) to (IV) has been previously reported, and its rate has been correlated with the internal energy of (III).[28]

Factor (iii) can be conveniently invoked to account for the increase of the relative extent of t-butylation which accompanies the decline of the absolute overall yield of alkylated products measured at increasing $[C_4H_8]$: [Arene] ratios (*cf.* Figure).

This interpretation, that accommodates the higher

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* In the n-butane chemical ionization spectra of arenes the ratio of protonated ($M + 1$) to butylated ($M + 57$) ions significantly *decreases* as the pressure is raised, and the trend is clearly apparent even in the very limited (0.1—0.5 Torr) range investigated. In addition, radiolytic alkylation of arenes in n-butane at 720 Torr yields s-butylarenes, as major reaction products, accounting for over 60% of the $C_4H_9^+$ reagent, irrespective of the proton affinity of the substrate (benzene, toluene, and *o*-xylene). This rules out reaction (6) as a predominant reaction channel. Finally, the abundance of $C_7H_7^+$ ions from the exothermic hydride ion abstraction from toluene, strictly similar to process (7), is <2% in the n-butane CI spectra of toluene, already at pressures of 0.3 Torr (ref. 10).

relative yields of t-butylxylene simply as a consequence of the preferential depletion of the more reactive s-$C_4H_9^+$ ions by the C_4 hydrocarbon, is consistent with the observation that, at any given $[C_4H_8]$: [Arene] ratio, the extent of t-butylation is higher from those C_4 hydrocarbons that give the lower overall yield of butylated products.

Finally, the higher reactivity of (III) with respect to (IV) in the addition process (3) is supported by the available high-pressure mass spectrometric data.[25]

Conclusions.—The gas-phase protonation of linear C_4 olefins and methylcyclopropane yields a charged alkylating reagent that promotes s-butylation and, to a minor extent, t-butylation of toluene and *o*-xylene. The s-butylating reagent displays a positional selectivity analogous to that typical of the s-butyl ions from n-butane.[10] t-Butylation becomes almost insignificant when the relatively mild $C_nH_5^+$ ions are used as the protonating reagent. The results can be rationalized by assuming that proton transfer to the linear C_4 alkenes and methylcyclopropane gives initially s-butyl ions, which undergo partial isomerization to the more stable tertiary structure. The extent of the isomerization depends on the excitation level of the $C_4H_9^+$ cations which in turn is determined by the exothermicity of the proton transfer process, in agreement with previous radiolytic and mass spectrometric results.* Protonation of isobutene yields exclusively t-butyl ions that show no tendency to isomerize, irrespective of the exothermicity of their formation. Protonation of cyclobutane promotes an alkylation process whose features, *i.e.* the positional selectivity and the s-butylation : t-butylation ratio, differ significantly from those typical of the reactions involving other C_4H_8 hydrocarbons. A possible explanation can be traced to the intervention of a different $C_4H_9^+$ moiety, perhaps protonated cyclobutane, whose occurrence in the gas phase had been previously reported.[27]

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* These conclusions apply to the uncatalysed isomerization of excited s-$C_4H_9^+$ ions, and do not conflict with recent results (ref. 15) on the isomerization of thermal ions, catalysed by *n*-type nucleophiles, in gaseous adducts. In the latter case, the isomerization rate increases with the adduct lifetime, and is therefore favoured by a lower exothermicity of its formation step.

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