The relationship ln (H/H_0)/ln $(D/D_0) = k_H/k_D$ was employed to calculate KSIE ratios in Tables III and IV, where $H = C_2H_4$, $D = C_2D_4$, etc. The runs in Table III indicated that ozonide product analysis could be used to estimate ethylene consumption. This method was used to develop Table IV, since recovery of ethylene was tedious. In this procedure, a 1:1 stoichiometry between ethylene and O_3 is assumed, and the relative deuterium content of nonozonide products is assumed to be identical with that in the ozonides. The relationship $(k_H/k_D)_{298} = (k_{C_2H_4}/k_{C_2D_4})^{T/298n}$ was employed to convert to a per deuterium basis at 25 °C. The scatter in the isotope ratios in Table IV (along with data from nine other reactions) leads to the listed uncertainty in the normalized KSIE ratio of about ±2%. The cross-ozonide fractions in Table V also resulted from the mass analysis.

H_2CO/D_2CO Insertion into CHD═CHD. The KSIE ratios in Table VI were determined with $k_{H_2CO}/k_{D_2CO} = (\text{oz-}d_1/\text{oz-}d_3)/(D_2CO/H_2CO)$. This should be a good approximation when the amounts of H_2CO and D_2CO are present in large excess or the extent of reaction is small. For the extents of reaction in Table VI, the D_2CO/H_2CO ratios decrease between 1 and 6% after ozonolysis. Hence, D_2CO/H_2CO was approximated as the median value during the reaction.

The amounts of oz-d_1 and oz-d_3 were determined by using mass spectral procedures similar to those described for the oz-d_4/oz-d_0 ratios. Fragmentation patterns for pure oz-d_4 were determined. Along with the data for oz-d_0 and oz-d_4, the necessary patterns for oz-d_1 and oz-d_3 were estimated by interpolation. This leads to expressions for the peak intensities between *m/e* 76 and *m/e* 79, corrected for ^{13}C contributions in terms of the amounts of d_1-, d_2-, and d_3-ozonides. The statistical deviations in the mass spectral data and ambiguities in determining the quantities of H_2CO and D_2CO and in estimating the effect of small amounts of C_2H_3D in the ethylene lead to accuracies of about ±4% in the normalized KSIE ratios.

Acknowledgments. Some initial experiments conducted by Dr. Kenneth Gallaher and Dr. Charles Gillies and discussions with Dr. Alexander Lopata aided aspects of this study. We are grateful to them and to the National Science Foundation which provided financial assistance (Grant CHE 76-09572). The NSF also provided a departmental equipment grant to computerize the mass spectrometry data system.

Aromatic Substitution in the Gas Phase. A Comparative Study of the Alkylation of Benzene and Toluene with $C_3H_7^+$ Ions from the Protonation of Cyclopropane and Propene

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Abstract: Gas-phase alkylation of benzene and toluene has been used as a probe to sample the isomeric population of $C_3H_7^+$ ions obtained from the protonation of cyclopropane and of propene, respectively, with H_3^+ ions in H_2 gas at pressures from 50 to 720 torr. The reagent from cyclopropane promotes extensive (over 40%) *n*-propylation, in addition to isopropylation of the arenes, in contrast to the reagent from propene that yields only traces of *n*-propylated products. The *n*-propylating reagent is identified as protonated cyclopropane, whose lifetime must exceed 10^{-7} s in the gaseous systems investigated. The mechanism and the selectivity of the gas-phase alkylation are discussed and compared to relevant mass spectrometric and kinetic results.

Introduction

The study of gas-phase aromatic substitution by carbenium ions generated in the dilute gas state with radiolytic techniques, or from the β decay of suitably tritiated precursors, has been reported in previous papers of this series.[1] In particular, the gas-phase reactions of methyl,[2-4] ethyl,[5] isopropyl,[6,7] and *tert*-butyl[8-10] ions with various arenes have been investigated, gathering direct information on the reactivity, selectivity, and steric requirements of free unsolvated carbenium ions.

The present paper is concerned with a comparative study of the reactivity of gaseous $C_3H_7^+$ ions obtained from two different sources, namely, by protonation of cyclopropane and of propene, respectively, in their gas-phase attack of benzene and toluene.

Apart from the intrinsic interest of the reaction that extends directly to the gas phase one of the most classical routes to the preparation of Friedel–Crafts alkylating reagents, it was hoped that contrasting the features of the two propylation processes could provide fresh evidence on the long-standing problem concerning the structure, stability, and interconversion rate of isomeric $C_3H_7^+$ ions in the dilute gas state.

Experimental Section

Materials. The gases employed (Ar, H_2, D_2) were high purity products from Matheson Co., whose stated purity exceeded 99.99 mol %. c-C_3H_6 and C_3H_6 were obtained from the same source, with a minimum purity of 99.0 mol %; O_2 and NH_3 were locally purchased research grade gases. C_6H_6 and C_7H_8 were gas chromatographic standards from Carlo Erba Co., while their alkylated derivatives, used for identification and calibration purposes in the GLC of reaction products, were either obtained from Fluka A.G. or prepared according to established procedures.

Procedure. The gaseous samples were prepared by standard vacuum techniques and introduced into 500-mL Pyrex ampules, equipped with break-seal tips, that had been previously evacuated to 10^{-5} torr and carefully outgassed. The vessels were sealed off and irradiated in a 220 Gammacell (Nuclear Canada Ltd.) at 34 °C at a dose rate of ca. 0.43 Mrad h^{-1} to total doses ranging from 2.2 to 17 Mrad, as determined by conventional Fricke dosimetry. Analysis of the products was carried out on a Sigma 1 gas chromatograph (Perkin-Elmer) equipped with a FID unit, using the following capillary columns: (i) a 300 ft × 0.020 in. stainless-steel column coated with Apiezon L grease, operated at a flow rate of 2.0 mL/min at 100 and 130 °C; (ii) a 150 ft × 0.010 in. stainless-steel column coated with Carbowax 20M, operated at a flow rate of 0.50 mL/min at 80 °C; and (iii) a 50 ft × 0.02 in. stainless-steel column, coated with poly(propyleneglycol), operated at a flow rate of 2.0 mL/min at 100 °C.

The products were identified by comparison of their retention volumes with those of authentic samples on at least two different columns, and their yields were deduced from the areas of the correspondent elution

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(1) For a recent review, cf. Cacace, F. In "Kinetics of Ion-molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, **1979**; p 199, and references cited therein.

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peaks, corrected for the individual response of the FID. The identity of the products was confirmed and their isotopic composition determined by GLC–mass spectrometry, using a Hewlett-Packard HP 5980 A instrument operated in the EI mode at an electron energy of 70 eV and a source temperature of 160 °C.

Results

Absolute Yields. The *absolute* yield of the alkylation, measured by the $G_{(+M)}$ values of the propylated arenes, can be approximately estimated from the amounts of products formed, the radiation dose, and the known[11] $G_{(+M)}$ values of the X_3^+ (X = H, D) ions formed within the system under the admittedly oversimplified assumption that all X_3^+ cations react with cyclopropane or propene to yield a correspondent number of $C_3H_7^+$ ions. In view of the approximate nature of the otherwise reasonable assumption (vide infra) and the rather large uncertainties affecting the calculation of the dose delivered to the irradiated gas, the $G_{(+M)}$ values reported must be regarded, at best, as crude estimates. Nevertheless their internal consistency is excellent, and they are of value to the present discussion in that they show that alkylation of arenes is indeed a major reaction channel in the systems investigated.

Thus, the combined $G_{(+M)}$ values of cumene and *n*-propylbenzene from the irradiation of X_2 gas containing traces of cyclopropane and benzene range from 0.70 to 1.20, depending on the composition of the system, in particular on the ratio $r = [C_6H_6]:[c\text{-}C_3H_6]$.

Within the range experimentally investigated, $0.10 < r < 0.30$, the overall $G_{(+M)}$ value for the propylation has been found to follow the linear equation

$$G_{(+M)} = 2.78r + 0.40$$

with a correlation coefficient of 0.983. Similar results have been obtained in the study of the $X_2/C_3H_6/C_6H_6$ systems. The alkylation of toluene invariably occurs with lower yields, using either cyclopropane or propene as a precursor of the $C_3H_7^+$ cations. As an example, the combined $G_{(+M)}$ values for the isomeric cymenes and *n*-propyltoluenes from the irradiation of X_2 at 720 torr, containing traces of toluene and cyclopropane in the molar ratio of 0.22, reached only 0.40, nearly one-half the value measured for the alkylation of benzene under comparable conditions. Finally, the ionic character of the alkylation process is demonstrated by the sharp decrease of the yields caused by the presence in the gas of a suitable base that intercepts the $C_3H_7^+$ reagent and its X_3^+ precursor. In a typical experiment, the $G_{(+M)}$ value of cumene drops from 0.96, in a system containing X_2 (720 torr), $c\text{-}C_3H_6$ (5 torr), and C_6H_6 (1.09 torr), to 0.13, measured in the same system containing, in addition, NH_3 at 10 torr, an exactly correspondent decrease being observed in the $G_{(+M)}$ value of *n*-propylbenzene.

Relative Yields. Isomeric and Isotopic Composition of Products. Once it is established that alkylation of arenes is a major reaction channel of the $C_3H_7^+$ ions from the protonation of both $c\text{-}C_3H_6$ and C_3H_6, a comparison of the *relative* yields, that can be measured with substantially greater accuracy than the *absolute* yields, is much more relevant to the specific purpose of a *comparative* investigation. Table I summarizes the results of a number of typical irradiations, giving the yield of each product as a percentage of the total amount of alkylated arenes formed and the ratio of *n*-propylation to isopropylation for both substrates.

The isomeric composition of the cymenes and *n*-propyltoluenes is illustrated in Table II together with the apparent k_T/k_B ratios deduced from competition experiments.

It is worth mentioning at this point that the ratio of *n*-propylation to isopropylation is determined by the composition of isomeric $C_3H_7^+$ ions *before the attack on the aromatic substrate*, since isomerization of *n*-propylarenium ions to isopropylarenium ions does not occur to any appreciable extent. This has been demonstrated by protonating *n*-propylbenzene with radiolytically formed H_3^+ ions in H_2 gas, under conditions similar to those prevailing in the alkylation experiments. No trace of iso-

Table I. Relative Yields of Alkylated Products

	system composition, torr								relative yields, %				ratios of yields	
													n-propylbenzene	*n*-propyltoluenes
expt	Ar	D_2	O_2	$c\text{-}C_3H_6$	C_3H_6	C_6H_6	C_7H_8	NH_3	cumene	*n*-propylbenzene	cymenes	*n*-propyltoluenes	cumene	cymenes
19		720	10	10		1.40			57^a	43			0.77	
16		720	10	7		0.72			57	43			0.77	
17		720^b	10	5		1.33			63	37			0.59	
32		720	5	5		1.09		10	61	39			0.62	
21		720	10	5			1.12				71	29		0.41
22		720	10	5		1.39	1.06		39	21	27	13	0.55	0.41
27		100^b	2	2		0.22			63	37			0.59	
28		100^b	2	2			0.17				74	26		0.36
29		50^b	1	1		0.12			61	39			0.62	
30		50^b	1	1			0.09				73	27		0.37
20		720	10		5	1.12			94	6			0.06	
24		720	10		5		1.64				93	7		0.07
23		720	10		5	1.42	1.21		58	4	34	3	0.07	0.09
9	600	100	10	5			1.21				65	35		0.52
12	600	100	10	5		1.11	1.10		43	25	20	12	0.59	0.59

[a] Standard deviation of data ≤ 10%. [b] H_2 used instead of D_2.

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Table II. Isomeric Composition of Cymenes and *n*-Propyltoluenes

expt	D_2, torr	C_3H_6	relative yields of cymenes, % ortho	meta	para	relative yields of *n*-propyltoluenes, % ortho	meta	para	k_T/k_B isopropylation	*n*-propylation
21	720	c-C_3H_6	29[a]	49	22	40	43	17	-	-
22	720	c-C_3H_6	36	44	20	43	37	20	0.9	0.8
28	100	c-C_3H_6	12	70	18	-[b]	-	-		
30	50	c-C_3H_6	4	85	11	-[b]	-	-		
24	720	C_3H_6	26	52	22	29	42	29	0.8	ca. 1.0
23	720	C_3H_6	30	44	26	-[b]	-	-		

[a] Standard deviation of data 5%. [b] Owing to the limited yields and traces of other products, the analysis of the isomeric composition of *n*-propyltoluenes in the low-pressure samples gave poorly reproducible data.

propylbenzene could be detected from these experiments.

The deuterium content of cumene and *n*-propylbenzene from systems containing D_2 as the bulk constitutent has been measured by combined GLC and mass spectrometry.

Irradiation of a system containing D_2 (720 torr), c-C_3H_6 (5 torr), C_6H_6 (1.06 torr), and O_2 (10 torr) gives a ratio of the monodeuterated to the unlabeled product of 91:9 for cumene and 42:58 for *n*-propylbenzene. Similar ratios, 87:13 for cumene and 41:59 for *n*-propylbenzene, have been measured in the products from a system containing D_2 (720 torr), c-C_3H_6 (10 torr), C_6H_6 (1.46 torr), and O_2 (10 torr). The isotopic composition of cumene from the irradiation of similar systems, containing propylene instead of cyclopropane, is significantly different in that the ratio of monodeuterated to unlabeled molecules is only 70:30.

Contrasting Features of Alkylation with Cyclopropane and with Propene. Comparison of the alkylating properties of the gaseous $C_3H_7^+$ reagents from the protonation of cyclopropane and propene leads to the following conclusions: (i) The absolute yields are very close. (ii) The ratio of *n*-propylation to isopropylation is markedly different, passing from 0.6–0.8 (cyclopropane) to 0.06 (propene) for benzene and from ca. 0.4 (cyclopropane) to ca. 0.08 (propene) in the case of toluene, with limited variations as a function of the pressure and the system composition. A remarkable feature is that *n*-alkylation is observed, if to a limited extent, also in the $H_2/C_3H_6/C_6H_5R$ systems. (iii) The isomeric composition of the cymenes is the same with both reagents, while that of *n*-propyltoluenes is appreciably different, with a much lower ortho:para ratio when propylene is used. The proportions of the meta isomer are higher in cymenes than in *n*-propyltoluenes. (iv) The isotopic composition of cumene from the D_2/c-C_3H_6 systems is characterized by a much higher degree of deuteration (91%) than from the D_2/C_3H_6 systems (70%). The deuterium content of the *n*-propylbenzene from the D_2/c-C_3H_6 systems is appreciably lower (42%).

Discussion

Alkylating Reagent. Irradiation of H_2, the bulk component of the gas, is known to yield H_3^+, a gaseous Brønsted acid, according to well-established processes (see eq 1 and 2).

$$H_2 \rightsquigarrow H_2^+ + e \tag{1}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{2}$$

These, and the following equations, are written for simplicity with unlabeled species, obvious modifications being in order whenever deuterated reagents are used. H_3^+ is also formed in the system containing excess Ar, but its ionic precursor is ArH^+ rather than H_2^+, and the exothermicity of the formation process is higher by some 30 kcal mol^{-1}. However, since the reagent must undergo a large number of unreactive collisions with H_2, or Ar, before encountering an organic molecule, complete thermalization can be expected in both cases, as shown by the close similarity of the observed reaction patterns. H_3^+ can exothermically protonate cyclopropane and propene according to reactions 3, whose

$$H_3^+ + \text{c-}C_3H_6 \rightarrow [C_3H_7^+]_{exc} + H_2 \tag{3a}$$

$$H_3^+ + C_3H_6 \rightarrow [C_3H_7^+]_{exc} + H_2 \tag{3b}$$

ΔH^0 values are approximately the same (−78 kcal mol^{-1}).[12,13]

Reactions 3 have been investigated by mass spectrometry at different pressures.[14] In H_2 gas at 0.1 torr, the large exothermicity of protonation causes extensive fragmentation, while a higher fraction of the propyl ions is collisionally stabilized at higher pressures (see eq 4).

$$[C_3H_7^+]_{exc} \rightarrow \text{fragments, i.e., } C_3H_5^+, C_3H_3^+, C_2H_5^+, \text{etc.} \tag{4a}$$

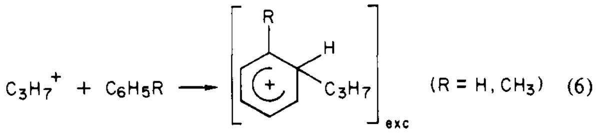
$$[C_3H_7^+]_{exc} \xrightarrow[-M^*]{+M} C_3H_7^+ \tag{4b}$$

Thus, at a H_2 pressure as low as 0.3 torr, $C_3H_7^+$ already becomes the major charged product, and there is little doubt that in the pressure range of interest in this work (50 to 720 torr) thermalyzed propyl ions are the only significant product from reactions 3. Indeed, quantitative formation of $C_3H_7^+$ from the protonation of cyclopropane and propene with a variety of gaseous acids, including H_3S^+,[15] $CH_3OH_2^+$, and $HC(OH)_2^+$,[13,16] has been repeatedly observed in the mass spectrometer. Unfortunately, little is known concerning the isomeric composition of the propyl ions from reactions 3 that can be reasonably expected to be appreciably different. The limited structural discrimination of mass spectrometry is at a particular disadvantage here, as propyl ions apparently undergo complete isomerization to the most stable structure in a much shorter time than required for application of diagnostic techniques such as collisional activation (CA). Thus, the CA spectra of the $C_3H_7^+$ ions (I) from the protonation of cyclopropane and of those (II) from the protonation of propylene are identical 10^{-5} s after their formation.[16] On the other hand, the ion–molecule reactions of I and II are still somewhat different 10^{-7} s after their formation,[16] and the $H_f°$ values of the two isomers are also different, 199.8 kcal mol^{-1} for I and 191.7 kcal mol^{-1} for II, as deduced from the PA of cyclopropane and propene.[13]

As a whole, the currently available data do not allow us to evaluate with any degree of confidence the isomeric composition of the propyl ions from reactions 3, especially if one considers the exothermicity of these reactions and the possibility of isomerization. It appears, however, that fast reactions with suitable nucleophiles, e.g., the arenes, may provide a probe to sample the population of $C_3H_7^+$ ions in the systems investigated.

Reactions of Propyl Ions. Exothermic reactions are possible with both major nucleophiles contained in the gas, namely, cyclopropane (propene) and the arenes (eq 5 and 6). The arenium

$$C_3H_7^+ + C_3H_6 \rightarrow C_6H_{13}^+ \xrightarrow{C_3H_6} \text{polymeric ions} \tag{5}$$



III

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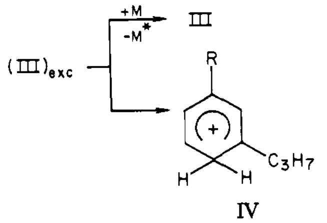
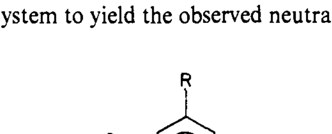
ions, excited by the exothermicity of the condensation[17,18] and unless collisionally stabilized, collapse to the most stable isomer (IV) (eq 7 and 8) before losing a proton to any gaseous base contained in the system to yield the observed neutral products (eq 9).



(7)

(8)

IV



(9)

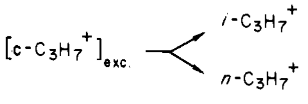
Besides consensation, other reaction channels are available to propyl ions, including exothermic hydride ion abstraction from toluene[12] (eq 10) and proton transfer to arenes (eq 11), exothermic from all isomeric propyl ions to toluene and from *n*-propyl ions to benzene as well.[12,13]

$$C_3H_7^+ + C_7H_8 \rightarrow C_3H_8 + C_7H_7^+ \qquad (10)$$

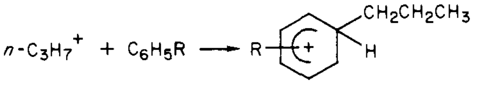
$$C_3H_7^+ + C_6H_5R \rightarrow C_3H_6 + C_6H_6R^+ \qquad (11)$$

It is worth mentioning that both competitive reactions 5 and 6 have been directly observed by high-pressure mass spectrometry. Chain condensation processes initiated by $C_3H_7^+$ cations have been demonstrated to occur in cyclopropane and, even more efficiently, in propylene in a study carried out at pressures up to 0.9 torr, where polymeric ions up to $C_{13}H_{25}^+$ have been detected.[19] Condensation between propyl ions and arenes also has been repeatedly reported following the first observation by Munson and Field.[20] From the calculated $G_{(+M)}$ value of $C_3H_7^+$ and the yields of propylated arenes, the competition between cyclopropane (propene) and benzene appears to be biased in favor of the arene, by a factor roughly estimated between 2 and 3, at least as far as the *alkylation* channel is concerned. Incidentally, the competition between channels 5 and 6 provides a neat explanation for the observed dependence of the $G_{(+M)}$ values of propylation on the $[C_6H_5R]:[C_3H_6]$ ratio.

Nature of *n*-Propylating Reagent from Cyclopropane. The most relevant result of the present investigation, i.e., the much higher ratio of *n*-propylation to isopropylation typical of the $C_3H_7^+$ reagent from cyclopropane with respect to that from propylene, can be explained by two alternative reaction sequences: (A) Isomerization of at least a fraction of protonated cyclopropane to *n*-propyl ions (eq 12a) followed by alkylation of the arene (eq 12b).

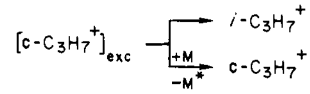


$$[c\text{-}C_3H_7^+]_{exc} \rightarrow i\text{-}C_3H_7^+ ,\; n\text{-}C_3H_7^+ \qquad (12a)$$

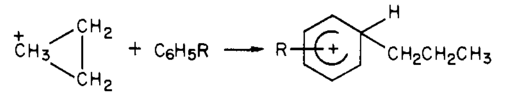


(12b)

(B) Survival of at least a fraction of protonated cyclopropane as such (eq 13) followed by nucleophilic attack of the arene that yields *n*-alkylated products (eq 14).



$$[c\text{-}C_3H_7^+]_{exc} \rightarrow i\text{-}C_3H_7^+ ;\; \xrightarrow[-M^*]{+M} c\text{-}C_3H_7^+ \qquad (13)$$



(14)

Sequence A is not unreasonable on energetic grounds in that the stability difference between $c\text{-}C_3H_7^+$ and $n\text{-}C_3H_7^+$ (ca. 8 kcal mol^{-1}) is indeed *smaller* than that between $i\text{-}C_3H_7^+$ and $n\text{-}C_3H_7^+$ (ca. 16 kcal mol^{-1}) according to currently accepted values.[13] Isomerization of excited $c\text{-}C_3H_7^+$ to $n\text{-}C_3H_7^+$ would therefore be *less unfavorable* than the corresponding process from comparably excited $i\text{-}C_3H_7^+$. However, several experimental features of the alkylation process are hardly compatible with sequence A. First, protonation of propylene by such an indiscriminate reagent as gaseous H_3^+ should yield directly $n\text{-}C_3H_7^+$ in addition to $i\text{-}C_3H_7^+$. In this case, it is difficult to explain why the primary ions from propylene do not survive long enough to promote *n*-propylation, as the $n\text{-}C_3H_7^+$ ions from $c\text{-}C_3H_6$ should do according to sequence A. In the second place, proton transfer (eq 11), that competes with alkylation, is energetically allowed *only* from $n\text{-}C_3H_7^+$ to C_6H_6 and from *both* $i\text{-}C_3H_7^+$ and $n\text{-}C_3H_7^+$ to C_7H_8. Consequently, if $n\text{-}C_3H_7^+$ were the alkylating reagent, the ratio of *n*-propylation to isopropylation should be *higher* for toluene, where *both* $i\text{-}C_3H_7^+$ and $n\text{-}C_3H_7^+$ undergo deprotonation (eq 11) in addition to alkylation (eq 6), than in C_6H_6, where only $n\text{-}C_3H_7^+$ ions are depleted by the competitive deprotonation process (eq 11). This is exactly the contrary of the experimental trend, as the observed ratio of *n*-propylation to isopropylation is actually *higher* for C_6H_6 (Table I).

The isotopic composition of alkylated products from the $D_2/c\text{-}C_3H_6/C_6H_6$ system, in particular the large (ca. 60%) fraction of unlabeled *n*-propylbenzene, is an additional diagnostic feature. The results can be easily accommodated by sequence B, since thermoneutral proton transfer from $c\text{-}C_3H_7^+$ to cyclopropane has been long demonstrated with tritiated reagents.[21,22] Competition of the process in eq 15 with reactions 5 and 6 provides a reasonable

$$c\text{-}C_3H_6D^+ + c\text{-}C_3H_6 \rightarrow c\text{-}C_3H_5D + c\text{-}C_3H_7^+ \qquad (15)$$

source of the required *unlabeled* *n*-propylating reagent in sequence B. On the contrary, it is difficult to account for the formation of unlabeled *n*-propylbenzene from sequence A, since *n*-propyl ions, the most unstable among $C_3H_7^+$ isomers, tend to be removed from the system rather than undergo isotopic scrambling with the large excess of cyclopropane. Thus, the proton transfer in eq 16,

$$n\text{-}C_3H_6D^+ + c\text{-}C_3H_6 \rightarrow C_3H_5D + c\text{-}C_3H_7^+ \qquad (16)$$

the counterpart of eq 15 in sequence A, exothermic by 16 kcal mol^{-1}, does not yield any unlabeled *n*-propyl ions but rather represents an effective sink that removes them from the system.[23]

Finally, a detailed study by Ausloos and co-workers[24] has demonstrated that *n*-propyl ions isomerize intramolecularly to isopropyl ions within 10^{-10} s, a much shorter time than that required for a reactive encounter with an arene molecule in the

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(17) Estimated to be ca. −29 kcal mol^{-1} for the isopropylation of benzene and −35 kcal mol^{-1} for the isopropylation of toluene, cf. ref 7.

(18) McLoughlin, R. G.; Morrison, J. D.; Traeger, J. C. *Org. Mass Spectrom.* **1979**, *14*, 104.

(19) Aquilanti, V.; Galli, A.; Giardini-Guidoni, A.; Volpi, G. G. *Trans. Faraday Soc.* **1968**, *64*, 124.

(20) Munson, M. S. B.; Field, F. H. *J. Am. Chem. Soc.* **1967**, *89*, 1047.

(21) Cacace, F.; Caroselli, M.; Cipollini, R.; Ciranni, G. *J. Am. Chem. Soc.* **1968**, *90*, 2222.

(22) Cacace, F.; Guarino, A.; Speranza, M. *J. Am. Chem. Soc.* **1971**, *93*, 1088.

(23) The almost complete (ca. 90%) deuteration of cumene from the $D_2/c\text{-}C_3H_6/C_6H_6$ system can be rationalized in the same way, as occurrence of the (slightly endothermic) process

$$i\text{-}C_3H_6D^+ + c\text{-}C_3H_6 \rightarrow C_3H_5D + c\text{-}C_3H_7^+$$

would simply remove isopropyl ions from the system without yielding unlabeled $i\text{-}C_3H_7^+$. On the other hand, thermoneutral proton transfer becomes again possible between $i\text{-}C_3H_7^+$ and propylene, and actually cumene formed from the $D_2/C_3H_6/C_6H_6$ system is partially (ca. 30%) unlabeled.

(24) Lias, S. G.; Rebbert, R. E.; Ausloos, P. *J. Am. Chem. Soc.* **1970**, *92*, 6430, and references cited therein.

systems investigated. Rearrangement to isopropyl ions was found to be favored under all conditions, but its rate further increases with increasing internal energy content of the ion,[23] a particularly significant feature in view of the highly exothermic character of process 3a.

As a whole, it can be concluded that the experimental results of this work and the available evidence from mass spectrometric and radiolytic studies exclude the role of n-$C_3H_7^+$ as a gas-phase n-propylating reagent in the systems investigated in favor of the longer-lived protonated cyclopropane.

Isomerization of Gaseous Arenium Ions and Substrate Selectivity. The isomeric composition of alkylated products from toluene is characterized by a large proportion of the meta isomer from the H_2/c-C_3H_6/C_7H_8 and the H_2/C_3H_6/C_7H_8 systems at 720 torr, the extent of meta substitution further increasing at lower pressures to a maximum value of 85% measured at 50 torr.

The positional selectivity measured in this work is undoubtedly affected by extensive isomerization of the primary arenium ions into the thermodynamically most stable meta isomer (IV), according to the process outlined in eq 7. The isomerization is much more pronounced than in gaseous hydrocarbons at comparable pressures. As a comparison, the isomeric composition of cymenes from the irradiation of C_3H_8 (720 torr), C_7H_8 (0.87 torr), and O_2 (10 torr) is 53% ortho, 27% meta, and 20% para, in good agreement with previously reported data.[6,7] The difference can be traced to the reaction environment, as collisional deactivation by H_2, the bulk constituent of the system, is undoubtedly less efficient than that by C_3H_8 at the same pressure. In addition, the average excitation level of the $C_3H_7^+$ ions when they undergo a reactive collision with C_7H_8 is conceivably higher in the present study, owing to the strongly exothermic character of reactions 3 and again to the comparatively less efficient collisional deactivation in H_2 gas.

The view that the observed composition of products is heavily affected by secondary isomerization is supported by the *lower* proportion of the meta isomer found in n-propyltoluenes with respect to cymenes under the same experimental conditions. This of course reflects the incipient ionic character of the migrating alkyl group in the transition state of the isomerization process, irrespective of its intramolecular or intermolecular nature, and the higher stability of free i-$C_3H_7^+$ with respect to n-$C_3H_7^+$.

Finally, no particular kinetic significance should be attached to the measured k_T:k_B ratio *lower* than unity. The ratio refers, in fact, exclusively to the alkylation channel rather than to the overall nucleophilic reactivity of the substrates. The lower alkylation rate of C_7H_8 can be traced to the competition of other processes, e.g., reactions 10 and 11, that affect exclusively, or predominantly, toluene with respect to benzene.

Conclusions

The propyl ions formed from the protonation of cyclopropane and propene, respectively, with H_3^+ display a significantly different reactivity toward arenes in that n-propylation is a major channel for the reagent from cyclopropane and a barely detectable one for that from propylene.

Evaluation of the main reaction features denies the role of n-$C_3H_7^+$ as the n-alkylating reagent and points to the intervention of protonated cyclopropane, whose lifetime must then exceed 10^{-7} s. These results are consistent with evidence previously derived from widely different sources. Existence of c-$C_3H_7^+$ had been inferred from experiments involving the decay of $^3H_2$, but the lower limit of the protonated cyclopropane lifetime must be set at only 10^{-10} s, owing to the composition and the pressure of the systems investigated.[21] Mass spectrometric measurements indicate that isomerization of c-$C_3H_7^+$ to i-$C_3H_7^+$ requires 10^{-5} to 10^{-7} s, an estimate[16] supported by the present results. Observation of gaseous $C_3H_7^+$ ions that react as protonated cyclopropane in hydride ion abstraction from alkanes has been reported in connection with radiolysis of n-C_4H_{10}/n-C_4D_{10} mixtures in the pressure range from 20 to 200 torr.[24] The minute but well-measurable yields of n-propylated arenes from the H_2/propene systems parallel the formation of traces of cyclopropane from the deprotonation of $C_3H_7^+$ ions from the radiolysis of propane,[25] indicating a (very limited) cyclization of originally linear cations.

Finally, the present results represent a direct extension to the dilute gas state of those typical Friedel–Crafts reactions that rely on the protonation of alkenes and cycloalkanes for the preparation of the alkylating reagent. It is worth noting in this connection that under conditions designed to reduce isomerization n-propylbenzene, formed via a process analogous to reaction 14, is the major product from the alkylation of C_6H_6 with cyclopropane in concentrated H_2SO_4.[26]

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"1,4" Alkyl Migrations in Fischer Indole Cyclizations

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Abstract: The product from Fischer indole cyclization and dehydrogenation of cyclohexanone 2,4,6-trimethylphenylhydrazone (**1**) was determined to be 2,3,4-trimethylcarbazole (**3**) resulting from a formal 1,4-methyl migration, as previously proposed. To determine the destinations of migrating groups in these rearrangements, the Fischer indole cyclization and dehydrogenation of cyclohexanone 2-ethyl-6-methylphenylhydrazone (**17**) were studied. The products obtained were 1-ethylcarbazole, 1-methylcarbazole, 2-ethyl-1-methylcarbazole (**18**), and an apparent mixture of 1-ethyl-4-methylcarbazole (**21**) and 4-ethyl-1-methylcarbazole (**22**). However, no 1-ethyl-2-methylcarbazole (**19**), which would have been obtained by a "1,4"-methyl migration, was obtained. Analysis of the product ratios suggested that the apparent [1,4] ethyl shift in formation of **18** actually proceeded by a formal [1,5] shift of either an ethyl or a methyl group, followed by a [1,2] ethyl shift. Cyclization of 3-pentanone 2,4,6-trimethylphenylhydrazone (**26**) proceeded to give the product of "1,4" methyl migration, demonstrating that such reactions can occur with phenylhydrazones of ketones other than cyclohexanone. It is proposed that steric factors play a major role in determining whether migrating groups undergo [1,2] or "1,4" shifts during Fischer indole cyclizations.

Migrating groups in rearrangements of butenyl carbonium ions may in principle undergo either [1,2] or [1,4] migrations (eq 1). The distances between the migration origins and the migration termini for most potential [1,4] migrations, however, would make

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