GAS-PHASE REACTIONS OF FREE PHENYLIUM CATIONS WITH C<sub>3</sub>H<sub>6</sub> HYDROCARBONS.<sup>1</sup>

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<u>Abstract</u> - Free, unsolvated phenylium ions formed by the spontaneous ß decay of a constituent atom of multitritiated benzene have been allowed to react with gaseous propene and cyclopropane in the pressure range from 10 to 700 torr. Phenylium ions attack efficiently both the C-H and the C-C bonds of cyclopropane, yielding respectively tritiated cyclopropylbenzene and indane as the major products. Selective attack of phenylium ions on the  $\pi$  bond of propene is suggested by the composition of tritiated products, isomeric phenylpropenes and isopropylbenzene. The different behavior of propene and cyclopropane toward gaseous phenylium ions is consistent with the results of related radiolytic investigations concerning gaseous systems at nearly atmospheric pressure. The reactivity pattern of the isomeric C<sub>4</sub><sub>6</sub> hydrocarbons toward gaseous phenylium ions is discussed and compared with pertinent mass spectrometric data.

The analogies existing in the chemical behavior of olefins and of their cyclopropane analogues toward electrophilic reagents, reflecting fundamental properties of the bonding in the C=C group and in the three-membered carbon ring,  $^{2-4}$  are well documented in solution.<sup>5</sup> A more direct correlation with theoretical models can be expected in ionic reactions occurring in the dilute gas state, unaffected by environmental factors such as solvation and ion pairing.

Such expectation is verified by the meagre experimental evidence on the reactivity of olefins and cyclopropanes toward gaseous cations, obtained with mass spectrometric and radiolytic techniques. As an example, the reactivity of propene and cyclopropane toward gaseous ethyl ions has been found to be substantially similar in a ICR experiment carried out with a Dempster-type mass spectrometer,<sup>6</sup> since the same species  $(C_{3}H_{7}^{+})$  is the major product from both substrates. However, the formation mechanism of the  $C_{3}H_{7}^{+}$  ions involves a competition between a direct protonation process and a condensation-elimination sequence whose relative rate is appreciably different in propene and cyclopropane. Although no detailed explanation of such difference is currently available, it is likely to arise from the energetic and structural features of the complex formed by the encounter of the ethyl ion with each  $C_{3}H_{6}$  hydrocarbon. More recently, appreciable differences in the reactivity pattern of the  $C_{3}H_{7}^{+}$  cations from the protonation of propene and cyclopropane in gaseous systems at pressures ranging from 50 to 720 torr have been demonstrated by radiolytic experiments.<sup>7</sup>

In this context, it was decided to undertake a comparative study of the reactivity of propene and cyclopropane toward suitable gaseous electrophiles, under conditions that allow the inference of the structure of the primary ionic products, and to detect their subsequent isomerization as a function of the environmental factors, in particular the pressure of the systems investigated. We believe that one of such reactants is the phenylium  $(C_6H_5^+)$  ion 1, which can be conveniently prepared in the dilute gas state by spontaneous  $\beta^{-1}$ nuclear decay of suitably multitritiated benzene precursors (eq. 1).<sup>8</sup> The choice of phenylium ion as the ionic electrophile is dictated by its unique property of having two active centers (the empty  $\sigma$  orbital and the  $\pi$ system), whose reactivity towards a number of simple alkanes, alkenes, and cycloalkanes, have been fully evaluated under low-pressure ICR conditions.<sup>9</sup>



## EXPERIMENTAL SECTION.

<u>interials</u>. The preparation, purification, and isotopic analysis of  $\begin{bmatrix} 1, 4-T_2 \end{bmatrix}$  and  $\begin{bmatrix} T_x \end{bmatrix}$ -benzene samples, used as the source of the phenylium ions, have been described elsewhere.<sup>8</sup> Cyclopropane, propene, annonia, and oxygen were research-grade gases from Matheson Gas Products Inc. and were used without further purification. Merck Co. provided all the research-grade aromatic compounds

4874

used as carriers or standards in the gas chromatographic analysis of the decay systems.

<u>Growth of Decay Products.</u> The experimental techniques used for the preparation of the samples have been described in full elsewhere.<sup>10</sup> From 1.0 to 1.4 mCi of multitritiated benzenes diluted with inactive benzene to a specific activity of 90 mCi mmol<sup>-1</sup>, were introduced into carefully evacuated and outgassed 250-500 mL Pyrex vessels, together with a measured amount of  $C_{3}H_6$  and  $0_2$  (4-10 torr), used as a radical scavenger. The vessels were, cooled with liquid nitrogen, then sealed off and stored at room temperature in the dark for 12-14 months.

<u>Analysis of the Products.</u> Two distinct procedures were followed for the analysis of the tritiated products from the decay systems. Measured aliquots of the homogeneous samples were subjected to radio glc analysis with the main purpose of estimating the absolute yields of tritiated products. A Model ACT/f C. Erba gas chromatograph was used, equipped with a hot-wire detector in series with a 10-mL internal-flow proportional counter from Berthold Laboratorium AG, heated at 175°C. The separations were carried out with helium as the carrier gas, the effluents being diluted with methane to a  $[CH_4]:[He]= 3:1$  ratio, before being passed through the proportional counter.

In most cases, the reaction vessels were opened and their content diluted with precisely weighed amounts of appropriate inactive carriers. After being throughly mixed, the samples were subjected to a preparative glc, in order to isolate and purify each radioactive component, the purification step being repeated until a constant value of the specific activity of each product was reached. The static radioactivity measurements were carried out with a liquid scintillation spectrometer, Model Tri-Carb 460 C, Packard Instrument Co.. The yield of each labeled product was deduced from the ratio of its activity to the total activity of the tritiated phenylium ions formed within the system during the storage period, as calculated from the initial activity of multitritiated benzene, its tritium content, and the known decay rate of tritium. The glc was carried out with the following columns: i- Bentone-34-SP 1200, 1.75%:5% on 100/120 Supelcoport, 5m, at 100°C; ii- Igepal ICO-880, 20% on 60/80 Chromosorb V, 5m, at 80°C.

## RESULTS.

When multitritiated benzene is allowed to decay in the presence of a large excess of gaseous  $C_{3}H_{6}$ , a variety of tritiated aromatic products is formed, whose absolute yields and relative distributions are reported in the Table. Relatively high yields (35-40%) of labeled  $C_{9}X_{10}$  (X = H, T) products are formed from the cyclopropane systems, and their distribution appears to depend significantly upon the total pressure of the sample. Low amounts (5%) of  $C_{9}X_{10}$  products are instead formed together with traces of ethylbenzene from the propene systems, in proportions substantially independent of their pressure. Most of the remaining activity in both systems is accounted for by gaseous and low-boiling fragmentation products and, especially in the case of propene, by

compounds (probably polymeric materials) which do not elute from the columns. It cannot be excluded that a hydride transfer from  $C_{3}H_{6}$  to phenylium ion gives tritiated benzene not discernible from undecayed starting  $C_{6}X_{6}$ .<sup>12</sup>

The ionic nature of the processes responsible for the formation of the tritiated products is ensured by the presence of an efficient radical scavenger, such as  $O_2$ , and confirmed by the strong depression of the yields caused by addition of NH<sub>2</sub>, an effective interceptor of gaseous cations.

The Table shows that indane and cyclopropylbenzene are the only significant products formed in  $c-C_{3H_6}^{H}$  at 700 torr. Their relative yields decrease significantly at lower pressures, in favor of monocyclic isomers, such as allyl- and isopropylbenzene, and <u>trans</u>-B-methyl-styrene. No tritiated indane and cyclopropylbenzene are formed in the propene systems, giving instead appreciable yields (47-50%) of <u>trans</u>-B-methyl-styrene, together with smaller amounts of **a**-methyl-styrene (20-22%), isopropyl- (14-23%) and allylbenzene (10-14%).

<u>TABLE.</u> Tritiated Product Distribution from The Gas-Phase Reaction of Phenylium Ion with  $C_3H_6$  Isomers.

System Composition <sup>a</sup>	Relative Yields of Products (%) <sup>b)</sup>						Absolute Yields (Activity, %) <sup>C)</sup>	
Substrate (torr)	0 <sub>2</sub> (torr)	J	9	5	6	6	5	
Cyclopropane (690)	10	55	45	n.d. <sup>d)</sup>	n.d.	n.d.	n.d.	40
Cyclopropane (100)	4	49	29	15	7	n.d.	n.d.	35
Cyclopropane (10)	4	6	46	28	n.d.	n.d.	20	36
Propene (110)	4	n.d.	n.d.	14	50	22	14	5
Propene (14)	4	n.d.	n.d.	10	47	20	23	5

a) The systems contained 1.0-1.4 mCi of multitritiated benzene (specific activity: 90 mCi  $mmol^{-1}$ ). The decay samples were stored in the dark, at room temperature, for 12-14 months. b) Expressed as a percentage of the total activity of the aromatic fraction of the tritiated products. Standard deviation of data, <u>ca.</u> 10%. c) Expressed as the percent ratio of the total activity of the end aromatic products to the activity originally contained in the nuclear-decay formed phenylium ion. d) n.d. = below detection limit ( < 0.5% absolute yield).

DISCUSSION.

Attack of Phenylium Ion on Cyclopropane. The nature and the properties of free phenylium ion produced by nuclear decay in tritiated benzene and used in the present study as the electrophilic reactant have been previously described.<sup>10</sup> Any reaction scheme for gas-phase attack of the phenylium ion on the chosen  $C_{3}H_{6}$  substrate should account for the specific nature of the electrophile and the nucleophilic centers available in the substrate. Thus, it seems likely that the primary interaction with  $c-C_{3}H_{6}$  involves the empty  $\sigma$  orbital of the phenylium ion and the C-H or C-C bonds of cyclopropane to give the three-centers-two-electron species 2 and 3, according to eq. 2. Owing to the presence of the  $\pi$ -system of the electrophile, the adducts 2 and 3 may rapidly evolve to the corresponding Wheland intermediates 4 and 5, excited by the exothermicity of their overall formation processes (eq. 2).<sup>13</sup>



Intervention of 4 is suggested by the recovery of significant amounts of cyclopropylbenzene (29-46%) under all conditions used. Concerning channel (2b), neither of the hypothetical intermediates involved, 3 or 5, can generate isolable bicyclic benzene derivatives without preliminary rearrangement to more stable isomers. Isolation of substantial quantities of indane at high pressure shows that the most efficient isomerization path for the intermediate species of eq. 2b is an intramolecular 1,2-CH<sub>2</sub> shift within the aromatic ring, probably promoted by relief of the strain energy in the aliphatic moiety of the



isomerizing intermediate(s). The  $CH_2$  group transfer leads to 6, the immediate ionic precursor of indane (eq. 3). The postulated isomerization step is analogous to the protonation-induced isomerization of alkylbenzenes, occurring <u>via</u> intramolecular 1,2 alkyl shifts, observed in the dilute gas state<sup>14</sup> as well as in solution.<sup>15</sup>

Even at the highest pressure (700 torr), collisional deactivation does not entirely prevent occurrence of the isomerization 5 - 6, although further structural rearrangement of 6 (and 4) appears completely inhibited. At lower pressures, collisional quenching of the excited intermediates 4 and 6 competes with isomerization or fragmentation processes yielding simpler species. Thus, appreciable yields of allylbenzene (15%) and trans- $\beta$ -methyl-styrene (7%) are formed at 100 torr, together with indane (49%) and cyclopropylbenzene (29%). The observed depletion of cyclopropylbenzene yield with respect to that measured at 700 torr suggests that one of the most significant isomerization pathways followed by the excited intermediates 2 and 4 is the proton transfer to the cyclopropane moiety,<sup>16</sup> preceding the formation of allylbenzene and trans-ß-methyl-styrene.



The composition of the products from the systems at 10 torr, where the decreased efficiency of collisional stabilization favours thermodynamic control, suggests occurrence of extensive isomerization, involving ring contraction within the excited intermediates 3 and 5 to give cation 7 and, following further H shifts, species 8.



While deprotonation of 7 by a gaseous base B (<u>e.g.</u> the cyclopropane itself) can account for the formation of allylbenzene, hydride-ion transfer to 8 from a suitable donor AH represents a likely route to isopropylbenzene.

In conclusion, the nature and the yields of the products formed at the highest pressure used, under conditions favoring <u>kinetic</u> control, suggest that phenylium ion efficiently attacks bond the  $\sigma_{C-H}$  and  $\sigma_{C-C}$  bonds of cyclopropane, with a slight preference for the bent C-C bonds.

Attack of Phenylium Ion on Propene. The reactivity pattern prevailing in propene differs substantially from that observed in gaseous cyclopropane. First, the much lower yields of labeled aromatic products obtained from the propene systems indicate that processes other than simple bimolecular condensation, e.g. hydride-ion abstraction, cationic polymerization, fragmentation, etc., are much more extensive. Second, the isomeric composition of the aromatic products does not depend much upon the pressure, at least within the range investigated (14-110 torr). Finally, indane and cyclopropylbenzene are not formed in propene under the conditions used. Instead, most of the activity is found in trans- $\beta$ -methyl-styrene, accompanied by minor yields of **q**-methyl-styrene, isopropyl- and allylbenzene.

The  $\pi$ -system of propene, characterized by a higher electron density represents the favoured site for the electrophilic attack of phenylium ion, yielding the  $\pi$ -adduct 9 which may conceivably evolve into the  $\sigma$ -intermediate 10 (eq. 6). The present results do not allow the establishment of the lifetime of



species such as 10, which may well respresent the direct precursors of the labeled aromatic products observed, either directly or following preliminary isomerization (eqs. 7 and 8).



4880

Under no circumstances does the direct attack of phenylium ion on propene yields products such as indane and cyclopropylbenzene, whose formation can be traced to cyclic intermediates 4 and 5, while the proportions of isomeric phenyl propenes formed from the two  $C_{3H_6}$  hydrocarbons lend support to the view that they arise from largely different populations of the same isomeric species. As a final consideration, it should be mentioned that, while phenylium ion attacks both the C-H and the C-C bonds of cyclopropane, it displays a distinct preference for the  $\pi$ -system of propene, over its  $\sigma$ -type centers, <u>e.g.</u> the C-H bonds, as shown by the relatively minor yields of allylbenzene with respect to the other products, and by the exclusive formation of the <u>trans</u> isomer of B-methylstyrene.

<u>Comparison with Mass Spectrometric Data.</u> A comparison of the present results with those obtained at much lower pressures by mass spectrometry must necessarily take into account the profound differences of the reaction environment. The major ion-molecule reaction 9 observed under typical ICR conditions occurs at nearly the same rate in propene and cyclopropane.<sup>9</sup>

$$C_{6}H_{5}^{+} + C_{3}H_{6} \longrightarrow C_{7}H_{7}^{+} + C_{2}H_{4}$$
 (9)

The low efficiency of collisional stabilization at pressures as low as  $10^{-5}$  torr allows in fact the excited intermediates from processes 2 and 6 to collapse into the thermodynamically most stable isomers, and to undergo the energetically allowed fragmentation process yielding  $C_7 H_7^+$  ions ans ethene.<sup>17</sup> Thus, the extensive secondary decomposition of the excited ionic intermediates largely obscures, under ICR conditions, the intrinsic differences in the reactivity of propene and cyclopropane toward  $C_6H_5^+$  ions, which become detectable only at much higher pressures, as those prevailing in the decay experiments, owing to the efficient stabilization of the  $C_{9}H_{11}^{+}$  primary adducts via multiple unreactive collisions with neutral molecules. The facile rearrangement and/or fragmentation of the excited  $C_{9}H_{11}^{+}$  intermediates suggested by the present results is consistent with the behavior of  $PhC_{3}H_{6}^{+}$  cations generated by electron impact in a double focusing mass spectrometer from a variety of precursors.<sup>18</sup> The ions generated from molecules containing three contiguous carbon atoms attached to a monosubstitued aromatic ring ungergo metastable decomposition leading to predominant (90-95%) loss of ethene. Furthemore, extensive isotopic randomization prior to ethene loss occurs in the ions from precursors containing a partially deuterated side chain. The metastable decomposition processes leading to loss of ethene become less significant in the ions formed from precursors containg a disubstituted or trisubstituted benzene ring. The excited adducts from the process investigated in a ICR spectrometer undergo predominat loss of ethene, preceded by extensive isotopic scrambling at low

$$c_{3}H_{5}^{\dagger} + c_{6}H_{6} \longrightarrow \left[c_{9}H_{11}^{\dagger}\right] exc \longrightarrow c_{7}H_{7}^{\dagger} + c_{2}H_{4}$$
 (10)

pressures.<sup>19</sup> However, when process 10 is studied under "high pressure"  $(10^{-2} \text{ torr})$  conditions, collisional deactivation prevents complete fragmentation of the excited  $C_{9}H_{11}^{++}$  adducts, thus allowing their direct detection. Such a trend underlines once again the profound effects of the reaction environment on the apparent reactivity of gaseous ions, and the care to be exercised when extrapolating and generalizing the results of purely mass spectrometric studies.

## CONCLUSIONS.

The phenylium ion displays a rich, if significantly different chemistry in gaseous propene and cyclopropane at pressures ranging from 10 to 700 torr. The structure of the products formed in cyclopropane gas at the highest pressure suggests insertion of the cation into the C-H and the C-C bond of the cycloalkane, giving initially bicyclic ions, that are collisionally stabilized and eventually yield indane and cyclopropylbenzene. At lower pressures, the primary bicyclic intermediates undergo partial isomerization to arenium ions containing a linear side chain. Ionic phenylation of propene is significantly different, both in the initial step and in the consecutive reactions of the primary intermediates.

The  $C_{6}H_{5}^{+}$  cation appears to attack predominatly the  $\pi$  bond of propene forming monocyclic ions that eventually evolve into isomeric phenylpropenes and isopropylbenzene. Apparently a major fraction of the primary adducts undergoes further reactions with propene, probably promoting a cationic polymerization chain, as suggested by the remarkably low yields of the  $C_{9}$  products isolated. The results of the decay experiments are not inconsistent with those of pertinent mass spectrometric studies, once the profound differences in the reaction environment are taken into account.

## ACKNOWLEDGHENT.

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REFERENCES AND NOTES.

(1) Gas-Phase Reactions of Arylium Ion with Hydrocarbons. Part. 2.

(2) De Meijere A., Angew. Chem. Int. Ed. Engl. 1979 18 809.

(3) (a) Walsh A.D., <u>Trans. Faraday Soc.</u> 1949 <u>45</u> 179; (b) Schoeller W.W., <u>Tetrahedron</u> 1973 <u>29</u> 929.

(4) (a) Förster Th., <u>Z. Phys. Chem. (Leipzig)</u> 1939 <u>B 43</u> 58.; (b) Coulson C.A., Moffit W.E., <u>J.</u> Chem. Phys. 1947 15 151; (c) Phil. Mag. 1949 40 1.

(5) (a) Charton M. in Zabricky J.: "The Chemistry of Alkanes", Interscience, London, 1970; (b)
Collins C.J., <u>Chem. Rev.</u> 1969 <u>69</u> 543; (c) Lee C.C., <u>Prog. Phys. Org. Chem.</u> 1970 <u>2</u> 129; (d) De
Puy C.H., <u>Fortschr. Chem. Forsch.</u> 1973 <u>40</u> 73; (e) De Puy C.H., Andrist A.H., Fünfschilling P.C.,
J. Am. Chem. Soc. 1974 <u>96</u> 948; (f) La Londe R.T., Debboli A.D., J. Org. Chem. 1973 <u>38</u> 4228.

(6) Fiaux A., Smith D.L., Futrell J.H., Int. J. Mass Spectrom. Ion Phys. 1977 25 281.

(7) Attinà M., Cacace F., Giacomello P., J. Am. Chem. Soc. 1980 102 4768.

(8) (a) Angelini G., Speranza M., Segre A.L., Altman L.J., J. Org. Chem. 1980 <u>45</u> 3291; (b)
Cacace F., Speranza M., Wolf A.P., Ehrenkaufer R., J. Labelled Compds. Radiopharm. 1982 <u>19</u> 905.
(9) Speranza M., Sefcik M., Henis J.M.S., Gaspar P.P., J. Am. Chem. Soc. 1977 <u>99</u> 5583

(10) (a) Speranza M. <u>Tetrahedron Lett.</u> 1980 <u>21</u> 1983; (b) Angelini G., Fornarini S., Speranza M., J. Am. Chem. Soc 1982 <u>104</u> 4773; (c) Fornarini S., Speranza M., J. Chem. Soc. Perkin Trans. II 1984 171.

(11) A substantial fraction of activity is present on the vessel walls, and cannot be easily removed by extraction with common solvents.

(12) Hydride-ion transfer from  $C_{3}H_{6}$  to  $C_{6}H_{5}^{+}$  ion is an energetically allowed process, irrespective of the structure of  $C_{3}H_{6}$  and of the  $C_{3}H_{5}^{+}$  ion produced, and the exothermicity ranging from -7 ( $C_{3}H_{6}$  = cyclopropane;  $C_{3}H_{5}^{+}$  = cyclopropyl cation) to -30 kcal mol<sup>-1</sup> ( $C_{3}H_{6}$  = propene;  $C_{3}H_{5}^{+}$  = allyl cation).

(13) Even under the unfavorable assuption that the proton affinity (PA) of the <u>ipso</u> position of cyclopropylbenzene is equal to that of benzene, <u>i.e.</u> = 183.7 kcal mol<sup>-1</sup> (Lau Y.K., Kebarle P., <u>J. Am. Chem. Soc.</u> 1976 <u>98</u> 7452), the exothermicity of process 2a reaches <u>ca.</u> -70 kcal mol<sup>-1</sup>. No similar approximate estimate can be made for eq. 2b. However, an enthalpy change close to that of eq. 2a can be reasonably expected. Within the limits of the  $\Delta H^{\circ}$  estimate for eq. 2a, the overall sequence 2b — 3 can be calculated to be exothermic by <u>ca.</u> 85-90 kcal mol<sup>-1</sup>.

(14) (a) Perez G., <u>J. Phys. Chem.</u> 1976 <u>80</u> 2983; (b) Cacace F., Giacomello P., <u>J. Chem. Soc.</u> Perkin Trans. II 1978 652.

(15) (a) Olah G.A., Schlosberg R.H., Porter R.D., 16 Y.K., Kelly D.P., Mateescu G.D., <u>J. Am.</u> Chem. Soc. 1972 <u>94</u> 2034; (b) Olah G.A., 16 Y.K., ibid 9241.

(16) The proton affinities of cyclopropane and propene are only 2.4 kcal mol<sup>-1</sup> lower than that of benzene (Yamdagni R., Kebarle P., <u>J. Am. Chem. Soc.</u> 1976 <u>98</u> 1320; Chong S.L., Franklin J.L., <u>J. Am. Chem. Soc.</u> 1972 <u>94</u> 6347).

(17) The overall exothermicity of the fragmentation process 9 is calculated to range from -54  $(C_7H_7^+ = \text{benzyl ion})$  to -63 kcal mol<sup>-1</sup>  $(C_7H_7^+ = \text{tropylium ion})$  for  $C_3H_6 = \text{cyclopropane}$ , and from -46  $(C_7H_7^+ = \text{benzyl ion})$  to -55 kcal mol<sup>-1</sup>  $(C_7H_7^+ = \text{tropylium ion})$  for  $C_3H_6 = \text{propene}$ , if  $\Delta H^o_f$  (benzyl ion) = 217 kcal mol<sup>-1</sup> and  $\Delta H^o_f$  (tropylium ion) = 208 kcal mol<sup>-1</sup>, Abboud J.L.M., Hehre W.J., Taft R.W., J. Am. Chem. Soc. 1976 <u>98</u> 6072.

(18) Uccella N.A., Williams D.H., J. Am. Chem. Soc. 1972 94 8778.

(19) (a) Houriet R., Elwood T.A., Futrell J.H., <u>J. Am. Chem. Soc.</u> 1978 <u>100</u> 2320; (b) Lay J.O., Jr., Gross M.L., <u>Ibid.</u> 1983 <u>105</u> 3445.