Reactions and Structures of Pentyl Ions from Isomeric Pentanes

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Abstract: The reactions of pentyl ions produced by ion–molecule reactions in the isomeric pentanes have been investigated by observing the ion–molecule reactions of the pentyl ions with additives (isobutylene, *tert*-butyl chloride, 2,5-dimethylhexane). Differences in reactivity can be attributed to differences in structure of the pentyl ions: *sec*-pentyl ions from *n*-pentane and *tert*-pentyl ions from isopentane and neopentane. Both secondary and tertiary ions were produced from $(CH_3)_2CDCH_2CH_3$, and the $C_5H_{10}D^+$ ions abstracted the tertiary deuterium from $(CH_3)_2CDCH_2CH_3$ to give the stable t-$C_5H_{11}^+$.

Mass spectrometric studies of ion–molecule reactions have been made for the lower alkanes: ethane, propane, the butanes, and the pentanes.[1-7] Radiolysis studies of ion–molecule reactions in the low molecular weight alkanes have also been done.[8,9] The most important products from ion–molecule reactions in these alkanes are the alkyl ions, $(M-H)^+$, produced by hydride transfer reactions. In particular, one obtains abundances of pentyl ions in the high pressure mass spectra of the isomeric pentanes much larger than those produced by electron ionization. These pentyl ions are formed in sufficient abundance that one may attempt to distinguish among their possible structures.

Previous studies have been done on butyl ions from the butanes by high pressure mass spectrometry[10,11] and radiolysis[9,12] which showed differences in reactivity between the butyl ions formed in isobutane and the butyl ions formed in *n*-butane. Since then, several studies have been made to differentiate and determine structures of oxygenated ions by differences in reactivity.[13-16] The purpose of the present study is to identify the pentyl ions formed by ion–molecule reactions in the isomeric pentanes.

One can intuitively assign a secondary structure to the pentyl ion from *n*-pentane formed by the reaction

$$CH_3CH_2CH_2CH_2CH_3 + R^+ \longrightarrow$$

$$RH + CH_3\overset{+}{C}HCH_2CH_2CH_3 \quad (1)$$

and a secondary or a tertiary structure to the ions from isopentane formed by the reaction

(1) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, 68, 3098 (1964).

(2) M. J. Henchman, H. T. Otwinowska, and F. H. Field, *Advan. Mass Spectrom.*, 3, 359 (1968).

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(8) G. G. Meisels, "Fundamental Processes in Radiation Chemistry," Interscience, New York, N. Y., 1968, pp 347–412.

(9) P. Ausloos, *Progr. React. Kinet.*, 5, 113 (1970).

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(12) P. Ausloos, S. G. Lias, and A. A. Scala, *Advan. Chem. Ser.*, No. 58, 264 (1966).

(13) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, 91, 2069 (1969).

(14) J. L. Beauchamp and R. C. Dunbar, *ibid.*, 92, 1477 (1970).

(15) M. L. Gross, *ibid.*, 93, 253 (1971).

(16) M. L. Gross and F. W. McLafferty, *ibid.*, 93, 1267 (1971).

$$CH_3CHCH_2CH_3 + R^+ \longrightarrow$$ (with CH₃ substituent)

$$\longrightarrow RH + CH_3\overset{+}{C}HCHCH_3 \quad (2a)$$
(with CH_3)

$$\longrightarrow RH + CH_3\overset{+}{C}CH_2CH_3 \quad (2b)$$
(with CH_3)

The neopentyl ion formed by hydride abstraction is expected to undergo a 1,2-methide shift to form the tertiary ion

$$(3)$$

or the *tert*-pentyl ion could be formed directly by a rearrangement in the intermediate complex.

With somewhat less confidence, one might expect that the more abundant structure present in isopentane at high pressures would be the tertiary ion, formed either by direct abstraction or by a rapid isomerization of the secondary ion. If the pentyl ions are identical in neopentane and isopentane, the reactivities of these two ions with added compounds should be the same. The reactivity of *sec*-pentyl ions from *n*-pentane should be different from the reactivity of the *tert*-pentyl ions.

Experimental Section

The instrument used primarily was a Bendix Model 12 TOF mass spectrometer modified for high pressure work and operated in the continuous mode.[17] The source pumping system consisted of a 600 l./sec Edwards diffusion pump with a CVC water cooled baffle and a 200 l./min Edwards forepump. The maximum source pressure obtained with the pentanes was 1 Torr. The pentanes and added reagents had stated purities of 99 mol % and were used without further purification. The 2-methylbutane-2-*d* was obtained from Merck Sharpe and Dohme of Canada, stated purity of 99.9%. No significant impurities were indicated in these experiments for any of the compounds. The gases were introduced from a glass manifold through a heated gold leak and metal tubing into the source reservoir. The manifold capacity was sufficient to maintain a constant source pressure (a decrease of less than 1%) for the duration of a mass spectrum. The gas mixtures were prepared volumetrically and allowed to equilibrate overnight to ensure complete mixing. Experiments were done over the pressure range from 0.020

(17) C. D. Miller, T. O. Tiernan, and J. H. Futrell, *Rev. Sci. Instrum.*, 40, 503 (1969).

Figure 1. Pentyl ions vs. pressure for isomeric pentanes.

Figure 2. Mixtures of pentanes with isobutylene.

to 0.60 Torr. Analyses up to 0.2 Torr were done with 70-V electrons. Above 0.2 Torr, 200-V electrons were used to increase the intensity of the ion beam. No further increase in sensitivity could be detected with electrons of energy above 300 V. The source temperature, read directly from a thermocouple connected to the source block, was kept at 100 ± 10°. The repeller was kept at 3 V which corresponds to a field strength of 5.4 V/cm. Pressure readings were taken from a thermocouple gauge connected directly to the back of the source reservoir. This thermocouple gauge was calibrated for each gas against a Texas Instrument quartz spiral Bourdon gauge.

For some of the experiments, a modified CEC-110B mass spectrometer was used.[18] The experiments were performed in the same manner with the two instruments and equivalent results were obtained.

Results and Discussion

Pentyl Ions. Figure 1 shows the pressure variation obtained with the Bendix mass spectrometer for the pentyl ions in the three isomeric pentanes. All of the ions produced by direct ionization decreased in the expected manner for these compounds, except for the butyl ions in neopentane which were unreactive over this pressure range. The only other prominent ion at high pressures was $C_5H_{10}^+$, formed by H_2^- transfer, about 10% of the total ionization in n- and isopentane. No ion of molecular weight greater than the ^{13}C isotope of the molecular ion, M^+, was observed. More than 60% of the total ionization for iso- and n-pentane at high pressures consisted of pentyl ions. The lower abundance of pentyl ions in neopentane is due to the nonreactivity of the butyl ions, as indicated by the invariance of the abundance of $I_{57}/\Sigma I_i$ with pressure. In each pentane, the pentyl ion is the predominant product which does not react with the pentanes to produce higher molecular weight products.

Qualitative agreement is observed between these data and previous results on neopentane at somewhat lower pressures.[2] The distributions of product ions are very different in this study in which the reactant ions are produced by electron ionization and in a recently reported photoionization study.[7] The differences, however, are due to the different distributions of reactant ions produced by the two techniques. The same patterns of reactivity are observed where comparisons can be made.

(18) (a) J. Michnowicz and B. Munson, *Org. Mass Spectrom.*, 4, 481 (1970); (b) J. Michnowicz, Ph.D. Thesis, University of Delaware, 1971.
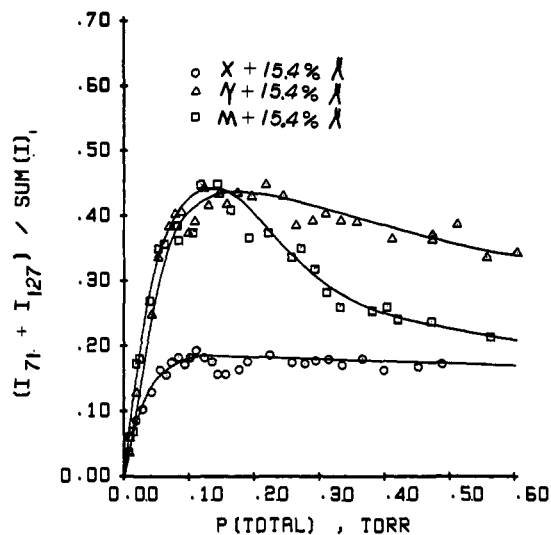
No discussion of rate constants is proposed in this paper.

Analyses of the reactivities of the pentyl ions with an additive were done by studying the pressure dependence of the abundances of pentyl ions in mixtures of each pentane with a small amount of the added compound. If the pentyl ion reacts with the additive its relative concentration (normalized to the total ionic abundance at each pressure) increases, passes through a maximum, and then decreases as the pressure is increased. If the pentyl ions do not react with the additive, the normalized abundance of $C_5H_{11}^+$ remains constant at higher pressures. Several polar and nonpolar additives were studied as mixtures with the pentanes. The compounds reported here showed pronounced differences in reactivity with pentyl ions obtained in the isomeric pentanes. Three types of reactions were used to differentiate among these pentyl ions: proton transfer, hydride transfer, and chloride transfer.

A. Proton Transfer. The results of the pressure studies of isobutylene–pentane mixtures are shown in Figure 2. Isobutylene provides a possible site for proton transfer

$$C_5H_{11}^+ + i\text{-}C_4H_8 \longrightarrow C_5H_{10} + t\text{-}C_4H_9^+ \qquad (4)$$

or a competitive addition reaction with the pentyl ions

$$C_5H_{11}^+ + i\text{-}C_4H_8 \longrightarrow C_9H_{19}^+ \qquad (5)$$
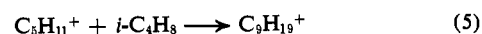
The mixtures reported in Figure 2 were 15.4 mol % i-C_4H_8 in each of the isomeric pentanes. In Figure 2 the sum of the abundances of the addition ion, $C_9H_{19}^+$, and the pentyl ion, $C_5H_{11}^+$, is plotted over the pressure range. This sum represents the unreacted pentyl ions and those which reacted by addition. No appreciable amounts of higher molecular weight ions were observed in these experiments. A maximum in the plot of $(I_{71} + I_{127})/\Sigma I_i$ must result from the competitive proton transfer reaction (4) and subsequent addition of butyl ions to i-C_4H_8. The pentyl ion concentration alone would pass through a maximum in each mixture because of reaction 5.

A noticeable difference in the reactivity of the pentyl ions with isobutylene can be seen in Figure 2. The pentyl ion produced from n-pentane reacts readily as

indicated by the curve for this mixture in which $(I_{71} + I_{127})/\Sigma I_i$ passes through a maximum and decreases at high pressures. This observation indicates that the pentyl ions are disappearing by proton transfer reactions (4). A necessary consequence of this proton transfer reaction which was observed, but is not shown, is the continuous increase over this pressure range of $(I_{57} + I_{113})/\Sigma I_i$, the sum of the abundances of the butyl ion and its addition product from the isobutylene–n-pentane mixture. The pentyl ions produced in neopentane indicate no proton transfer since the sum $(I_{71} + I_{127})/\Sigma I_i$ maintains a constant value at high pressures.

This difference in reactivity can be attributed to differences in structures of the pentyl ions. The $C_5H_{11}^+$ ions produced by ion–molecule reactions in n-pentane transfer a proton to isobutylene, an exothermic reaction if secondary ions react to give tertiary ions.[19-21] Since the energetics of the formation of pentyl ions are about the same for the two pentanes, the failure to observe proton transfer from the pentyl ions in neopentane must indicate a different structure, probably the expected tertiary ion.

The small, 5%, decrease in the abundance of pentyl and addition ions in the isopentane mixture may be real and may indicate the presence of two types of pentyl ions. The lack of a major effect indicates that the pentyl ions produced in isopentane are different from the pentyl ions produced in n-pentane. Since rapid proton transfer is expected from the secondary ions produced in reaction 2a and is observed for the secondary ions produced by (1) in n-pentane, the low reactivity suggests that the pentyl ions in isopentane are predominantly tertiary ions.

B. Hydride Transfer. Figure 3 shows the results of the reactions of the pentyl ions in mixtures of the isomeric pentanes with 10% 2,5-dimethylhexane. This higher molecular weight branched hydrocarbon provides two tertiary positions for hydride abstraction by pentyl ions

$$C_5H_{11}^+ + C_8H_{18} \longrightarrow C_5H_{12} + C_8H_{17}^+ \qquad (6)$$
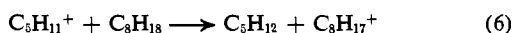
Hydride transfer is observed for the pentyl ions produced from ion–molecule reactions in n-pentane. The normalized abundance of pentyl ions passes through a maximum and decreases above 0.2 Torr. Also, $I_{113}/\Sigma I_i$ was the continuously increasing function of pressure necessary to establish reaction 6. This reaction is expected if the pentyl ions formed in n-pentane have the secondary structure, since abstraction of a tertiary hydrogen by a secondary carbonium ion should be exothermic.

In the isopentane and neopentane mixtures no reaction of the pentyl ions is seen. Rate constants for hydride transfer reactions of *tert*-butyl ions with branched hydrocarbons have been determined by radiolysis experiments.[19] The rate constants are essentially zero unless a tertiary hydrogen is removed and are 3–10 × 10^{-11} cc/(molecule sec) depending on the nature of the hydrocarbon. The hydride transfer reaction of t-$C_4H_9^+$ (from isobutane) with 2,2,4-trimethylpentane is much slower than the hydride transfer reaction of

(19) P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, **92**, 5037 (1970).
(20) J. H. Futrell and T. O. Tiernan, *Science*, **162**, 415 (1968).
(21) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and J. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **26** (1969).
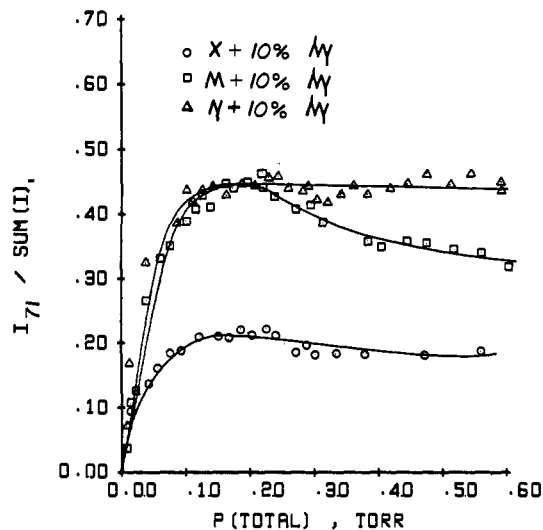
Figure 3. Pentyl ions in mixtures of pentanes with 2,5-dimethylhexane.

sec-$C_4H_9^+$ (from n-butane) with 2,2,4-trimethylpentane.[10] Rapid reactions of secondary alkyl ions to abstract both secondary and tertiary hydrogens have been observed in mass spectrometric studies.[20] From the known heats of formation of the lower primary alkyl ions,[21,22] we would expect that hydride abstraction by a primary neopentyl ion (if present) would be exothermic and rapid. In recent radiolysis studies, neutral products have been observed which are attributed to rapid hydride abstraction reactions of primary alkyl ions.[23]

Consequently, it seems reasonable because of these differences in reactivities of the pentyl ions to assign the secondary structure to the pentyl ions formed in n-pentane and the tertiary structure to the pentyl ions formed in neopentane and isopentane. From the constancy of $I_{71}/\Sigma I_i$ at high pressures, we estimate that less than 10% of the pentyl ions in isopentane would have the secondary structure.

C. Chloride Transfer. Figure 4 shows the pressure dependence of the relative abundance of pentyl ions in mixtures of each of the pentanes containing 10 mol % *tert*-butyl chloride. As in the previous two cases, the differences in reactivities of pentyl ions of n-pentane and of isopentane and neopentane are very apparent.

Associated with the marked decrease in $I_{71}/\Sigma I_i$ at high pressures in the n-pentane–*tert*-butyl chloride mixture is a continuous increase in I_{57}. These observations clearly establish the chloride transfer reaction

$$C_5H_{11}^+ + t\text{-}C_4H_9Cl \longrightarrow t\text{-}C_4H_9^+ + C_5H_{11}Cl \qquad (7)$$
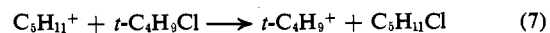
The constancy of $I_{71}/\Sigma I_i$ at high pressures for isopentane–*tert*-butyl chloride mixtures and for neopentane–*tert*-butyl chloride mixtures shown in Figure 4 shows the absence of an analogous Cl^- transfer reaction for the pentyl ions formed from these pentanes. If the pentyl ions from isopentane had the secondary structure or if the pentyl ions from neopentane had the primary structure, we would expect rapid Cl^- transfer reactions to give the low energy t-$C_4H_9^+$.

(22) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).
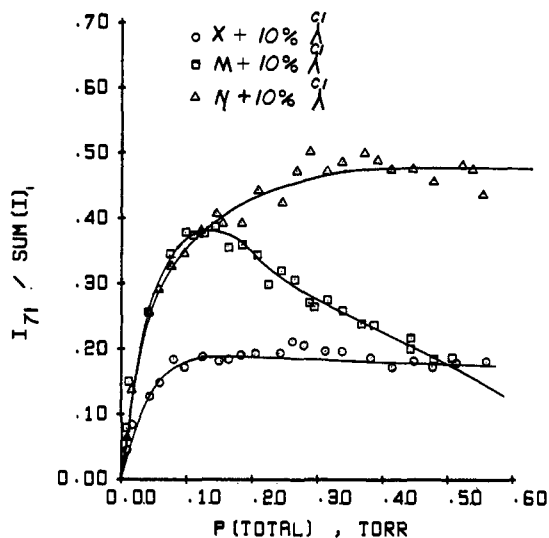(23) S. G. Lias, R. E. Rebbert, and P. Ausloos, *J. Amer. Chem. Soc.*, **92**, 6430 (1970).

Figure 4. Pentyl ions in mixtures of pentanes with *tert*-butyl chloride.

Figure 5. Pentyl ions in $(CH_3)_2CHCH_2CH_3$ and $(CH_3)_2CDCH_2$-CH_3.

These observations are consistent with the previous assignments of the secondary structure to the pentyl ions from *n*-pentane and the tertiary structure for the pentyl ions from iso- and neopentane. From the lack of reaction of $C_5H_{11}^+$ ions from isopentane with *tert*-butyl chloride, we again estimate that less than 10% of the pentyl ions could have the secondary structure.

The results of these experiments can be summarized briefly. The pentyl ion formed by ion–molecule reactions in *n*-pentane is predominantly *sec*-$C_5H_{11}^+$, an ion which readily reacts with appropriate substrates to form tertiary ions by proton, hydride, or chloride transfer reactions. The isomerization of *sec*-$C_5H_{11}^+$ to *t*-$C_5H_{11}^+$ is slow compared with the reaction time, which is of the order of a microsecond.

The pentyl ion formed by ion–molecule reactions in neopentane is *t*-$C_5H_{11}^+$, an ion which does not undergo rapid proton, hydride, or chloride transfer reactions.

The pentyl ions produced by ion–molecule reactions in isopentane are predominantly *t*-$C_5H_{11}^+$ ions which do not undergo rapid proton, hydride, or chloride transfer reactions. However, from these experiments we can say nothing about the transitory existence of secondary ions formed by reaction 2a and the proton transfer experiments shown in Figure 2 suggests the possibility of some reactive pentyl ions formed in isopentane.

Figure 5 shows the pressure variation of the abundances of pentyl ions for 2-methylbutane and 2-methylbutane-*2-d*. The abundance of the pentyl ions at *m/e* 72, $C_5H_{10}D^+$, has been corrected for the ¹³C isotope of pentyl ions at *m/e* 71, $C_5H_{11}^+$. The ionic abundance at *m/e* 71 has not been corrected for the pentene ions formed in this mixture by H_2^- transfer. This correction will be neglected since $C_5H_{10}^+/C_5H_{11}^+$ = 0.15 for isopentane over the pressure range 0.2–0.5 Torr.

Two important observations may be made from this curve: both H^- abstraction to give *m/e* 72 and D^- abstraction to give *m/e* 71 occur at approximately equal rates and the *m/e* 72 species clearly reacts to produce
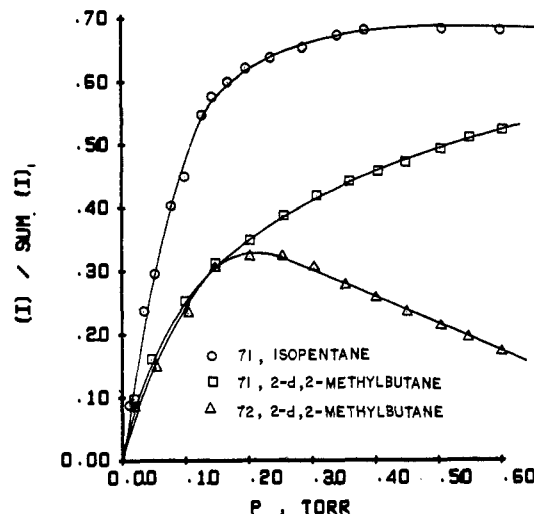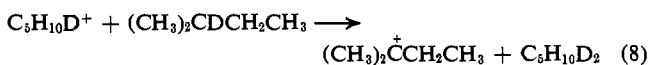
the species at *m/e* 71. The species at *m/e* 71 is *t*-$C_5H_{11}^+$ produced by direct abstraction of the tertiary deuterium, and the species at *m/e* 72 should be initially $(CH_3)_2CD\overset{+}{C}HCH_3$ produced by abstraction of one of the secondary hydrogen atoms.

The maximum in the curve for $C_5H_{10}D^+$ in Figure 5 implies the hydride transfer reaction

$$C_5H_{10}D^+ + (CH_3)_2CDCH_2CH_3 \longrightarrow$$
$$(CH_3)_2\overset{+}{C}CH_2CH_3 + C_5H_{10}D_2 \quad (8)$$

Thus, the secondary $C_5H_{10}D^+$ ions, $CH_3\overset{+}{C}HCD(CH_3)_2$, unless isomerization occurs, abstract a deuterium to give a more stable tertiary ion. At high pressures, therefore, all of the pentyl ions produced by ion–molecule reactions will have the expected tertiary structure after times in the order of microseconds.

Since the isomerization of these secondary ions to the tertiary structure involves only a 1,2-hydride shift, this isomerization reaction may be much more rapid than the slow (compared with 10^{-6} sec) isomerization of *sec*-butyl to *tert*-butyl ions or *sec*-pentyl to *tert*-pentyl ions which is not observed when these ions are produced by ion–molecule reactions. The resulting tertiary ion would necessarily possess excess internal energy, which might well be sufficient to effect the observed hydride transfer reaction.

Analyses of mixtures of $(CH_3)_2CDCH_2CH_3$ with added compounds provided no conclusive information about this possible isomerization reaction.

Significant concentrations of butyl ions are produced in each pentane which allow observation of their reactivity with the pentanes. From their reactivities butyl ion structure assignments can be made which are in agreement with other methods of analysis. The *sec*-butyl ion is predominant in *n*- and isopentane.[12,21,22] The *tert*-butyl ion is predominant in neopentane.[19,21,24]

(24) S. G. Lias and P. Ausloos, *J. Chem. Phys.*, 43, 2748 (1965).