Gaseous Ionic Alkylation

M. S. B. Munson[1]

Contribution from the Baytown Research and Development Division,
Esso Research and Engineering Company, Baytown, Texas.
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Abstract: By the technique of high-pressure mass spectrometry it has been possible to observe some of the elementary steps involved in alkylation. Collision-stabilized addition of butyl and other alkyl ions to several olefins was noted. The $C_8H_{17}^{+*}$ intermediate complexes formed from t-$C_4H_9^+$ and *sec*-$C_4H_9^+$ with the isomeric butenes appear to be different. The differences in some cases appear to be due to differences in structure. Highly branched octyl ions can be formed by ion–molecule reactions, but the stabilities of the ions are very sensitive to their energy content or method of formation.

For several years work has been done in these laboratories on the reactions of ions from hydrocarbons and related materials. Ionic reactions and ionic intermediates are important in the petroleum industry and in organic chemistry in general, and useful information about ionic processes has been obtained from mass spectrometric studies such as these in which the complications of solvation are not present. The experimental conditions within the source of a mass spectrometer are very different from those in ionic solutions, but neither an accurate molecular picture nor the current description involves the state of aggregation. Differences between gaseous and solution processes may indicate specific solution effects which should be considered more carefully.

The historical development of the study of gaseous ion–molecule reactions has been twofold: to increase the pressures at which the reactions take place so that the extrapolation to more normal conditions is believable and multiple collision processes may be observed; and to obtain more detailed information on the reactions through increasingly clever and complex instrumentation which enables the states of the ions to be determined more precisely. Although more and more complex molecules are being studied, the molecules are still simple from the point of view of an organic chemist.

The experiments to be reported in this paper—reactions of butyl ions from butane or isobutane with olefins—were undertaken because of the importance of alkylation reactions to the petroleum industry. The work is an effort to study in detail the elementary ionic reactions and to observe any correspondence between gaseous and solution processes. The alkylation reactions of interest

$$C_xH_{2x+1}^+ + C_nH_{2n} \xrightarrow{(M)} C_{n+x}H_{2(n+x)+1}^+ \qquad (1)$$

require a third body for stabilization and hence pressures of several tenths to a few torr in order to be observed.

The results from these high-pressure experiments are not as clear-cut as those obtained from two stage mass spectrometers with incident beams of known mass, because the origin of the ions of low concentration can seldom be determined. However, the major reactions of the abundant ions can be determined, particularly if the experiments are arranged so that the major ions do not react with the major component, and collision-stabilized reactions can readily be observed.

The instrument and experimental procedure have been adequately described previously.[2] The butane and isobutane were Phillips Research Grade hydrocarbons (stated purity 99.95+ mole %) for which no successful further purification was achieved. The purity of all of the other hydrocarbons, C_3H_6, 1-C_4H_8, t-2-C_4H_8, i-C_4H_8, 1-C_5H_{10}, 2,2,4-trimethylpentane, and 2,4,4-trimethylpentene, was greater than 99%. The electron energy was approximately 800 v; the source temperature 200 ± 10°; and the repeller, 5 v corresponding to a field strength of 12.5 v/cm.

Results and Discussion

Butyl ions are the major product ions in both butane and isobutane and the butyl ions do not react with butane to any appreciable extent to give further products; that is, the relative concentration of butyl ions is substantially constant in each butane for pressures from 0.5 to 1.5 torr (the highest pressure of these experiments). These reactions have been discussed previously.[3,4] It has been demonstrated that if a product ion does not react with the neutral molecules from which it is formed, one can observe reactions with other species by studying mixtures with small amounts of added materials.[5–7] The major reactions of the primary ions will not be drastically altered, and the majority of the reactions which will be observed will be those of the butyl ions which do not react with butane. Since the predominant species are *sec*-$C_4H_9^+$ in butane and t-$C_4H_9^+$ in isobutane,[7] the two butanes will be discussed separately.

Butane and Butane–Olefin Mixtures. Figure 1 shows plots of the relative abundances of butyl ions as functions of pressure for *n*-butane and mixtures of *n*-butane with a few per cent olefins. The nonreactivity of butyl ions with butane is shown in this graph. There are appreciable differences in the reactivities of the *sec*-butyl ions with these olefins. Values for the rate constants for the reactions of these butyl ions with the ole-

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(1) Address inquiries to Department of Chemistry, The University of Delaware, Newark, Del. 19711.

(2) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

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

(4) M. S. B. Munson, *J. Phys. Chem.*, in press.

(5) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 4242 (1965), and earlier papers.

(6) M. S. B. Munson and F. H. Field, *ibid.*, **89**, 1047 (1967), and earlier papers.

(7) M. S. B. Munson, *ibid.*, **89**, 1772 (1967).

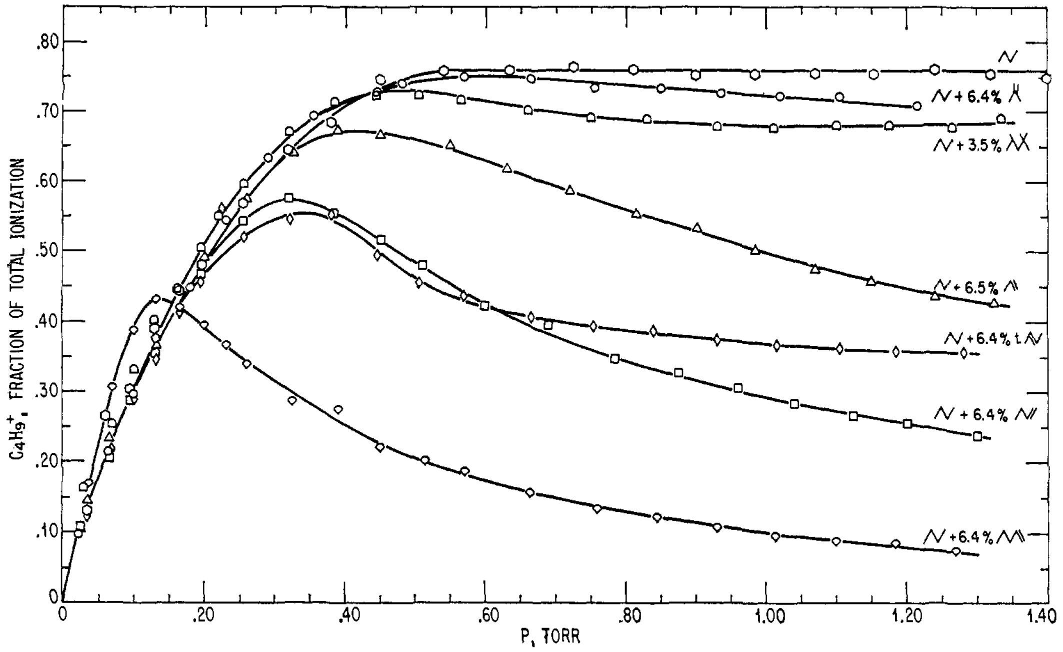

Figure 1. Butyl ion concentration *vs.* *P* for n-C_4H_{10} and mixtures with n-C_4H_{10}.

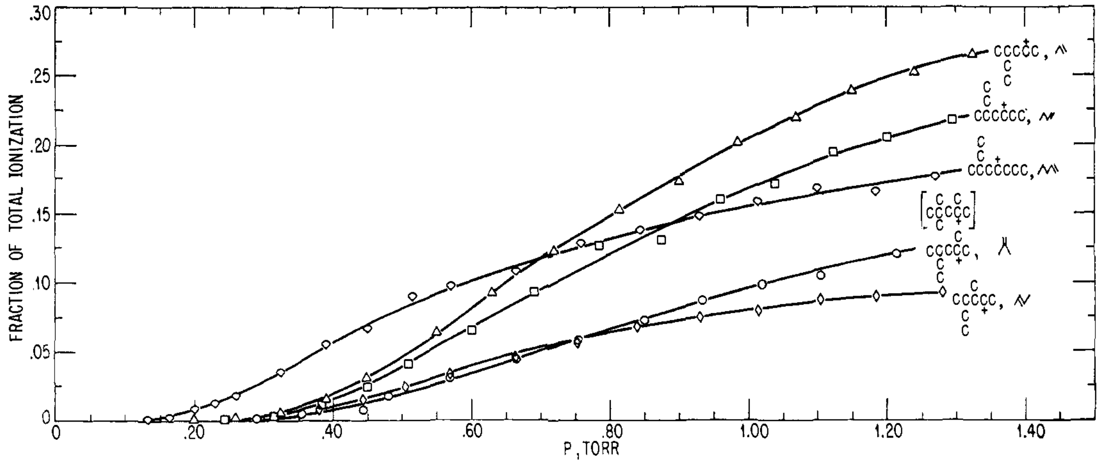

Figure 2. Alkylation products of *sec*-butyl ions in butane–olefin mixtures.

fins can be estimated from plots of log $(I_i/\Sigma I_t)$ *vs.* *P* in the high-pressure region from 0.4 to 1.2 torr. The residence times are not known accurately in these experiments at high pressures, but with the assumption that they are approximately the same as the zero pressure values calculated from simple electrostatics, one may estimate the rate constants. The most obvious regularity within this group is shown for the 1-olefins; propylene, $k \simeq 3.2 \times 10^{-10}$ cc/molecule sec; 1-butene, $k \simeq 5.7 \times 10^{-10}$ cc/molecule sec; and 1-pentene, $k \simeq 10 \times 10^{-10}$ cc/molecule sec. This increase in rate constant is in the order of increasing polarizability for this homologous series. The relative values should be reliable even if the absolute values are in error.

As will be discussed later, t-$C_4H_9^+$ reacts slowly with i-C_4H_8 so the small rate constant for the mixture with isobutylene may be attributed in part to a proton transfer reaction from *sec*-$C_4H_9^+$ to i-C_4H_8 to give t-$C_4H_9^+$, a reaction which is approximately 15 kcal/mole exothermal. The semilog plot for t-2-butene does not give a good straight line, so other reactions must be occurring. The apparently slow reaction with 2,2,4-trimethylpentane is surprising since H^- abstraction to give a tertiary carbonium ion is exothermic. One explanation that is consistent with but not established by these experiments is that the octyl ions produced by reaction of butyl ions with 2,2,4-trimethylpentane dissociate to give butyl ions again. Previous experiments on the chemical ionization mass spectra of paraffins suggested that the highly branched alkyl ions dissociated into lower molecular weight alkyl ions when the alkyl ions were produced by CH_5^+ and $C_2H_5^+$.[8]

Figure 2 shows the relative concentrations of the alkylation product ions from reaction in these mixtures. The structures are written assuming that the addition of the butyl ions occurs according to the usual conventions, and rearrangements are ignored. The second possibility for reaction with isobutylene results from the likelihood that some t-butyl ions are formed and react. There are appreciable differences in the extent of alkylation, and one may easily see that the extent of

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[8] F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 167.

reaction of butyl ions and the formation of alkylation ions do not parallel each other. For example, butyl ions react approximately three times as fast with 1-pentene as with propylene, but notably more heptyl ions are produced in the mixture with propylene than nonyl ions in the mixture with 1-pentene. To facilitate the discussion each compound will be considered separately.

Propylene. The sum of the relative concentrations of $C_4H_9^+$ and $C_7H_{15}^+$ is essentially constant from 0.4 to 1.3 torr, varying only from 0.69 to 0.72. $C_7H_{15}^+$ increases with a higher power dependence on the pressure than $C_4H_9^+$, approximately fourth. This value is sufficiently close to the relative concentration of butyl ions in butane, 0.76, that the formation of heptyl ions must be the dominant process for the loss of butyl ions in this mixture.

$$C_4H_9^+ + C_3H_6 \rightleftarrows C_7H_{15}^{+*} \qquad (2a)$$

$$C_7H_{15}^{+*} + C_4H_{10} \rightleftarrows C_7H_{15}^+ + C_4H_{10}^* \qquad (2b)$$

Precise rate constants cannot be calculated for this reaction sequence, so it is not possible to be quantitative about other processes which might result from decomposition of the excited $C_7H_{15}^+$ intermediate. The data indicate that the alkylation reaction 2 is a collision-stabilized reaction requiring participation of at least one other molecule and is not simple addition.

Decomposition of the excited heptyl ion to give $C_4H_9^+$ of the same or different structure may occur, but it is not detectable in the present experiments. $C_7H_{13}^+$ is formed as a monotonically increasing function of pressure, maximum concentration of 2% of the total ionization; and the ratio $(C_7H_{15}^+)/(C_7H_{13}^+)$ increases linearly with increasing pressure. Consequently, it seems reasonable that $C_7H_{13}^+$ is formed from the decomposition of the excited complex formed in (2a).

$$C_7H_{15}^{+*} \longrightarrow C_7H_{13}^+ + H_2 \qquad (2c)$$

Only about 1% of the total ionization is in the form of $C_5H_{11}^+$ ions even at the highest pressures of these experiments, so it cannot be a major product from the decomposition of $C_7H_{15}^{+*}$. In addition, the ratio $(C_7H_{15}^+)/(C_5H_{11}^+)$ increases more than linearly with increasing pressure, so it seems likely that $C_5H_{11}^+$ is formed from a reaction of one of the primary ions of butane with propylene.

Since the rate of disappearance of $C_3H_7^+$ ions in this mixture is substantially the same as it is in butane,[4] the proton transfer reaction is negligible. This statement

$$C_4H_9^+ + C_3H_6 \not\longrightarrow C_3H_7^+ + C_4H_8 \qquad (3)$$

is equivalent to saying that the $C_7H_{15}^{+*}$ complex in (2a) does not decompose appreciably to give propyl ions. The rate constant for (3) is at least a factor of 10 slower than the hydride transfer reaction which accounts for the disappearance of $C_3H_7^+$

$$C_3H_7^+ + C_4H_{10} \longrightarrow C_4H_9^+ + C_3H_8 \qquad (4)$$

for which $k = 4 \times 10^{-10}$ cc/molecule sec.[4] Indeed, there is no evidence for the occurrence of (3) in these experiments.

The only other ion of consequence which might come from the decomposition of the $C_7H_{15}^{+*}$ complex is $C_6H_{13}^+$ with a maximum concentration of 4% of the total ionization. However, it is unlikely that this ion is formed from $C_7H_{15}^{+*}$ because the neutral product would be CH_2 and the process should be endothermic no matter what the structure of the $C_6H_{13}^+$ ions. The ratio $(C_7H_{15}^+)/(C_6H_{13}^+)$ is definitely nonlinear with pressure.

The hexyl ion is surely formed at least partially from the alkylation of propylene with the propyl ion

$$C_3H_7^+ + C_3H_6 \rightleftarrows C_6H_{13}^{+*} \qquad (5a)$$

$$C_6H_{13}^{+*} + C_4H_{10} \longrightarrow C_6H_{13} + C_4H_{10}^+ \qquad (5b)$$

Although it is not possible to be quantitative, the existence of this concentration of hexyl ions indicates that both of the second-order rate constants must be of the order of 10^{-10} to 10^{-19} cc/molecule sec since (5a) competes with (4) for which $k = 4 \times 10^{-10}$ cc/molecule sec and the ratio of butane to propylene is 15.

Only trace amounts of higher alkylation products were observed (less than 0.5% of the total ionization), and the values were too erratic for useful discussion.

1-Butene. The ionic distribution in the 1-butene–butane mixture as a function of pressure is more complicated than in the butane–propylene mixture: $C_4H_9^+$, 26%; $C_5H_{11}^+$, 25%; $C_8H_{17}^+$, 20%; $C_8H_{15}^+$, 3%; $C_9H_{19}^+$, 2% at 1.2 torr. As was shown in Figures 1 and 2 the butyl ion reacts more rapidly with 1-butene than with propylene, but less alkylation occurs. This difference is the result of competing dissociations of the $C_8H_{17}^{+*}$ complex. The reactions appear to be

$$C_4H_9^+ + 1\text{-}C_4H_8 \rightleftarrows$$

$$C_8H_{17}^{+*} \begin{cases} \longrightarrow C_5H_{11}^+ + C_3H_6 & (6a) \\ \longrightarrow C_8H_{15}^+ + H_2 & (6b) \\ \xrightarrow{C_4H_{10}} C_8H_{17}^+ & (6c) \end{cases}$$

The ratio $(C_8H_{15}^+)/(C_5H_{11}^+)$ is reasonably constant with a value of 0.1 in the high-pressure region. $C_6H_{13}^+$ and $C_7H_{15}^+$ are present as less than 1% of the total ionization. The formation of this amount of $C_5H_{11}^+$ accounts for roughly half of the loss of $C_4H_9^+$ at 1 torr. It also appears that some $C_5H_{11}^+$ is formed by lower order processes (reactions of primary ions with 1-C_4H_8) since there is relatively more $C_5H_{11}^+$ than expected in the pressure region below 0.5 torr. This observation is not surprising, since some of the primary ions should react with 1-butene, but it is not possible to sort out the reactions.

Alkylation products of propyl ions were observed with propylene, but there is much less $C_7H_{15}^+$ ($\leq 0.7\%$) in this mixture than $C_6H_{13}^+$ in the mixture with propylene (3.8%). Consequently, the alkylation of 1-butene by propyl ions is slower than the alkylation of propylene by propyl ions because the propyl ion and olefin concentrations are the same. It is very likely that this difference is the result of the competing proton transfer reaction to give butyl ions.

More $C_4H_7^+$ ions are formed in this mixture (3%) than in butane (1%), undoubtedly as the result of H^- transfer reactions between the primary ions and 1-butene. $C_4H_7^+$ reacts with butane and the maximum in the plot of concentration *vs.* pressure occurs at about 0.3 torr in pure C_4H_{10}. The maximum value for $C_4H_7^+$ in this mixture also occurs at about 0.3 torr and the concentration of $C_4H_7^+$ is negligibly small for pressures above 0.6 torr. There is no evidence for the occurrence of H^- transfer reactions between $C_4H_9^+$, $C_5H_{11}^+$, or $C_8H_{17}^+$ and 1-butene.

$C_9H_{19}^+$ is formed to the extent of about 2% of the total ionization at 1.3 torr, presumably from alkylation of 1-butene with pentyl ions. This amount of $C_9H_{19}^+$ corresponds to approximately 10% conversion of the pentyl ions at this pressure. Consequently, the alkylation of 1-butene by these pentyl ions is approximately as fast as the alkylation of 1-butene with butyl ions, certainly different by less than a factor of 10.

1-Pentene. The system of butane and 1-pentene is even more complicated than the butane and 1-butene system since appreciable concentrations of C_4, C_5, C_6, C_9, C_{10}, and small concentrations of C_{11} alkyl ions are present. For example, at 1 torr there is 26% $C_5H_{11}^+$, 15% $C_9H_{19}^+$, 10% $C_4H_9^+$, 10% $C_6H_{13}^+$, 7% $C_{10}H_{21}^+$, and 1% $C_{11}H_{23}^+$. The major reactions appear to be

$$\begin{array}{l} C_4H_9^+ + C_5H_{10} \rightleftarrows \\ \qquad C_9H_{19}^{+*} \left\{ \begin{array}{lr} \longrightarrow C_5H_{11}^+ + C_4H_8 & (7a) \\ \longrightarrow C_6H_{13}^+ + C_3H_6 & (7b) \\ \xrightarrow{C_4H_{10}} C_9H_{19}^+ & (7c) \end{array} \right. \end{array}$$

$C_7H_{15}^+$ is present only as a maximum of 1% of the total ionization at 1.3 torr and $C_8H_{17}^+$ is never greater than 0.7%. $C_5H_{11}^+$ and $C_6H_{13}^+$ appear to be third-order ions which react further and the ratio $(C_6H_{13}^+)/(C_5H_{11}^+)$ is approximately one-third independent of pressure from 0.2 to 1.3 torr. The variation of this ratio below 0.2 torr may be attributed to reactions of primary ions with 1-C_5H_{10} which give primarily $C_5H_{11}^+$. The ratios $(C_9H_{19}^+)/(C_6H_{13}^+)$ and $(C_9H_{19}^+)/(C_5H_{11}^+)$ increase at least linearly with increasing pressure, so $C_9H_{19}^+$ cannot be formed by a simple bimolecular collision.

The relative concentrations of both $C_5H_{11}^+$ and $C_6H_{13}^+$ pass through broad maxima as the pressure is increased and C_{10} and C_{11} alkyl ions are formed at the higher pressure. Therefore alkylation reactions of the pentyl and hexyl ions also occur with 1-pentene. At 1.3 torr the concentration of $C_{19}H_{21}^+$ (8.4%) corresponds to 25% conversion of pentyl ions and the concentration of $C_{11}H_{23}^+$(1%) corresponds to about 8% conversion of the hexyl ions. The ratio $(C_{11}H_{23}^+)/(C_{10}H_{21}^+)$ is substantially constant at 0.11, an observation which suggests that these ions are formed by reactions of the same kinetic order. Since the ratio of hexyl to pentyl ions is about one-third, the alkylation of 1-pentene by hexyl ions proceeds about one-third as fast as the alkylation of 1-pentene with pentyl ions. Approximately 25% of the butyl ions have been converted to nonyl ions at 1.3 torr. The kinetics are different so precise comparisons cannot be made, but these results indicate that the alkylation reactions of butyl, pentyl, and hexyl ions with 1-pentene proceed at roughly the same rate.

There is much less $C_8H_{17}^+$ in this mixture of 1-pentene and butane (<0.7%) than there is $C_6H_{13}^+$ in the mixture of butane and propylene (3.8%), so that alkylation of 1-pentene with propyl ions is much slower than the alkylation of propylene with propyl ions. This difference is likely due to the competing proton transfer reaction of propyl ions to give pentyl ions. These observations are essentially the same as those reported for the mixtures of 1-butene.

$C_5H_9^+$ is formed at a maximum concentration of 3% as a second-order ion which reacts further. The maximum concentration occurs at 0.2–0.3 torr, but the concentration of $C_5H_9^+$ is still 1% at 1.3 torr, so it is possible that a small amount of $C_5H_9^+$ may be formed by H^- transfer reactions of the higher alkyl ions with 1-pentene, but these data do not provide strong evidence for this reaction.

***t*-2-Butene.** The reactions in this mixture of 2-butene and butane are similar in some respects to those in the mixture of butane and 1-butene. At 1.2 torr the relative concentrations are $C_4H_9^+$, 36%; $C_5H_{11}^+$, 23%; $C_8H_{17}^+$, 9%; and $C_8H_{15}^+$, 5%. The major reactions of the butyl ions appear to be

$$\begin{array}{l} C_4H_9^+ + 2\text{-}C_4H_8 \rightleftarrows \\ \qquad C_8H_{17}^{+*} \left\{ \begin{array}{lr} \longrightarrow C_5H_{11}^+ + C_3H_6 & (8a) \\ \longrightarrow C_8H_{15}^+ + H_2 & (8b) \\ \xrightarrow{C_4H_{10}} C_8H_{17}^+ & (8c) \end{array} \right. \end{array}$$

and the ratio $(C_8H_{15}^+)/(C_5H_{11}^+)$ is about 0.19 in this mixture with 2-butene and 0.10 in the mixture with 1-butene. Essentially no C_6 or C_7 alkyl ions are produced. The low concentration of $C_7H_{15}^+$ (0.5%) in this mixture compared with 3.8% for $C_6H_{13}^+$ in the mixture with propylene means that the alkylation of 2-butene by propyl ions is much slower than the alkylation of propylene by propyl ions. A similar observation was made about the alkylation of 1-butene with propyl ions. As was noted with 1-butene, there is no evidence for H^- abstraction reactions of pentyl or octyl ions with 2-butene.

There are, however, notable differences in the extent of alkylation of these two butenes which indicate that the $C_8H_{17}^{+*}$ intermediate complexes in (6) and (8) are different—a difference in structure, surely, since their energy contents are essentially the same. At 1.3 torr in the mixture of butane and 6.4% 1-butene the relative concentration of $C_8H_{17}^+$ was 22% of the total ionization, and in this mixture of butane and 6.4% 2-butene the relative concentration of $C_8H_{17}^+$ is only 9% of the total ionization. Another difference is in the rates of reaction of $C_4H_9^+$. For this mixture with 2-butene, a plot of log $(I_{57}/\Sigma I_i)$ *vs.* P was not a good straight line, but taking a fit to the data one obtains a value of 3×10^{-10} cc/molecule sec for the rate constant for the reaction of $C_4H_7^+$ with 2-butene, approximately one-half the value for 1-butene. The shape of the curve for the concentration of $C_4H_9^+$ as a function of pressure is much flatter in the high-pressure region than one would expect, and this qualitative observation suggests some reaction which forms butyl ions, perhaps decomposition of the octyl ions, and an approach to a pseudo-equilibrium.

Another difference worthy of note is that in this mixture the maximum concentration of $C_9H_{19}^+$ ions is 0.1% at 1.3 torr, but in the mixture with 1-butene the maximum concentration of $C_9H_{19}^+$ was 2.3% at 1.3 torr. The alkylation of 2-butene by pentyl ions is, therefore, much slower than the alkylation of 1-butene. Unfortunately the structure of the reactant pentyl ions cannot be established.

Isobutylene. The similarity between the reactions in this mixture of *n*-butane with 6.4% *i*-C_4H_8 and the reactions in the mixtures with the other two butenes is that both $C_5H_{11}^+$ and $C_8H_{17}^+$ are formed, apparently by the same processes. Quantitatively, however, there are very large differences: a maximum of 7% $C_5H_{11}^+$

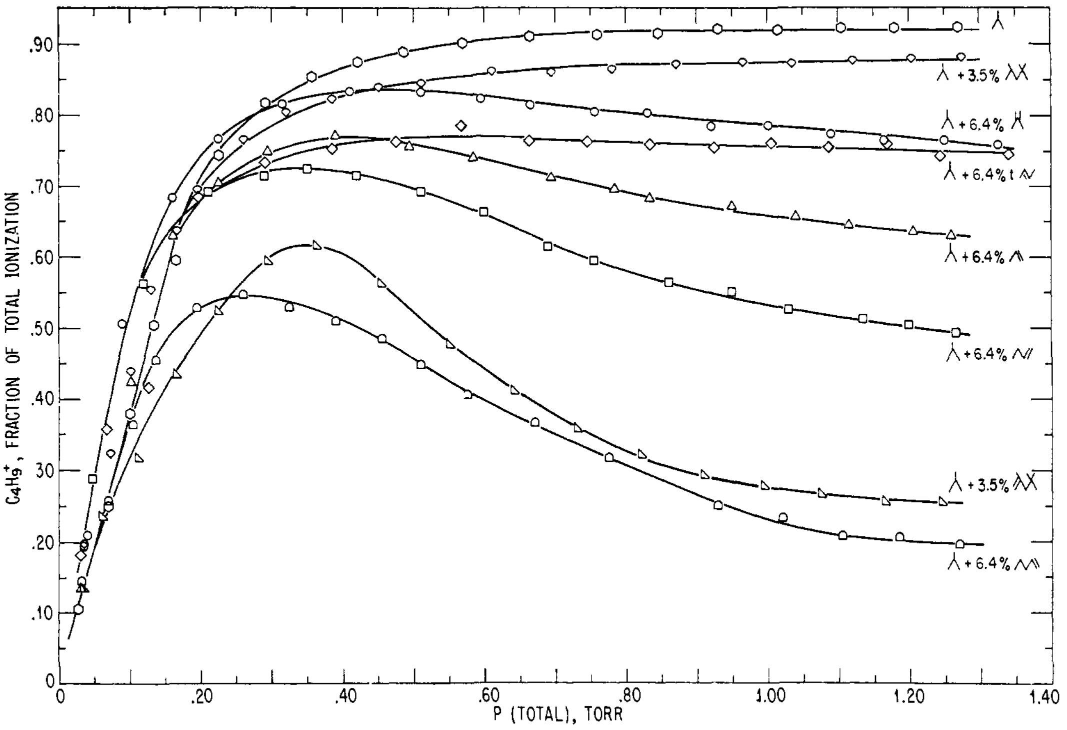


Figure 3. Butyl ion concentrations *vs.* *P* for i-C_4H_{10} and mixtures with i-C_4H_{10}.

in this mixture compared with 23–25% with the other butenes and a rate constant for the disappearance of $C_4H_9^+$ in this mixture of 0.5×10^{-10} cc/molecule sec, one-tenth of the rate constant for reaction with 1-butene. The concentration of octyl ions is 12% at 1.2 torr compared with 9% for 2-butene and 22% for 1-butene. It is readily apparent that the $C_8H_{17}^{+*}$ excited intermediates are different for the addition of butyl ions to these three butenes. Since the heats of formation of these three complexes are essentially the same, the differences are likely due to differences in structures.

The maximum concentration of $C_5H_{11}^+$ occurs at about 0.6 torr (7.2%) and the concentration of $C_5H_{11}^+$ decreases gradually as the pressure is increased further and at 1.2 torr it is 4%. This behavior indicates that $C_5H_{11}^+$ reacts, but alkylation does not occur since the relative concentration of $C_9H_{19}^+$ ions is never greater than 0.2% of the total ionization. Since $C_9H_{19}^+$ ions are not formed from reactions of $C_5H_{11}^+$ with isobutylene, the $C_9H_{19}^{+*}$ intermediate complex must be dissociating to give t-$C_4H_9^+$ by proton transfer since no other ions are formed.

No evidence is obtained for H^- transfer reactions of $C_5H_{11}^+$ or $C_8H_{17}^+$ with i-C_4H_8. Alkylation of i-C_4H_8 by propyl ions is also negligible since $C_7H_{15}^+$ is never greater than 0.3% of the total ionization.

Isobutane and Isobutane–Olefin Mixtures. Figure 3 shows the relative concentrations of butyl ions as functions of pressure for isobutane and several mixtures of isobutane with olefins. The nonreactivity of the butyl ions with isobutane is shown by the constant value for $C_4H_9^+$ in pure isobutane for pressures above 0.6 torr. There are several obvious similarities to the reactions in the mixtures of n-butane with these olefins. The same regularity is observed in the rates of reaction of t-butyl ions with propylene, 1-butene, and 1-pentene ($k = 1.4$, 2.7, and 7.0×10^{-10} cc/molecule sec, respectively) that was observed for reactions of *sec*-butyl ions from n-butane. All three of these rate constants are smaller than the rate constants for reactions of *sec*-butyl ions with the same compounds.

Figure 4 shows the relative concentrations of alkylation products in these mixtures. A comparison with Figure 2 will show appreciable quantitative differences in the extent of alkylation, particularly in the relative amounts of C_7, C_8, and C_9 alkyl ions formed in the mixtures with propylene, 1-butene, and 1-pentene.

Propylene. The only products of consequence for the butyl ions in this mixture of isobutane and 6.4% propylene are hexyl and heptyl ions. Essentially no pentyl ions are formed and $C_7H_{13}^+$ is never greater than 0.5% of the total ionization. The maximum concentration of hexyl ions is 7.2% in this mixture although it is about 3.8% in the n-butane–propylene mixture. The maximum concentration of propyl ions is 30–33% for both mixtures and the rate constants for reaction with butane and isobutane are both about 4×10^{-10} cc/molecule sec. Part of the $C_6H_{13}^+$, therefore, is probably formed from some reactions other than alkylation of propylene by propyl ions. There is a somewhat smaller amount of alkylation of propylene by butyl ions in this mixture (17%) than in the n-butane–propylene mixture (26%), a difference which parallels the difference in reactivity of the two butyl ions.

1-Butene. The major products of ionic reactions in this mixture are $C_5H_{11}^+$ (10%), $C_7H_{15}^+$ (1.2%), $C_8H_{15}^+$ (1%), $C_8H_{17}^+$ (23%), and $C_9H_{19}^+$ (1.6%) at 1.3 torr. In a manner analogous to the reactions of *sec*-butyl ions with 1-butene, the reactions appear to be

$$t\text{-}C_4H_9^+ + 1\text{-}C_4H_8 \rightleftarrows$$

$$C_8H_{17}^{+*} \begin{cases} \longrightarrow C_5H_{11}^+ + C_3H_6 & \text{(9a)} \\ \longrightarrow C_8H_{15}^+ + H_2 & \text{(9b)} \\ \xrightarrow{C_4H_{10}} C_8H_{17}^+ & \text{(9c)} \end{cases}$$

These results may be compared with the product distributions in n-butane–1-butene mixtures under the

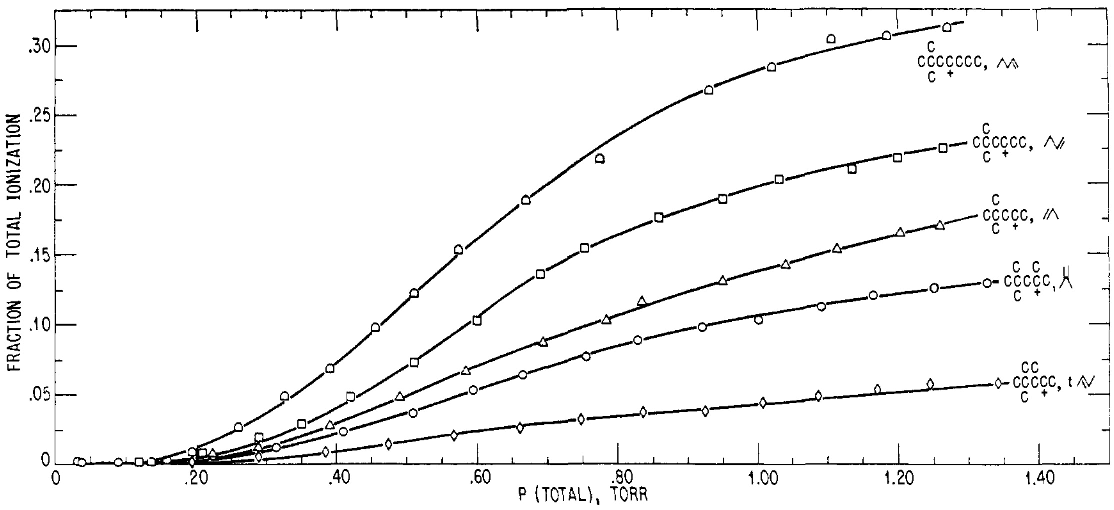


Figure 4. Alkylation products of *t*-butyl ions in *i*-C_4H_{10}–olefin mixtures.

same conditions: $C_5H_{11}^+$ (25%), $C_8H_{15}^+$ (3%), and $C_8H_{17}^+$ (22%). The differences in $C_5H_{11}^+$ concentrations are sufficiently great to indicate differences in the $C_8H_{17}^{+*}$ intermediate complexes.

The pentyl ions react further to give nonyl ions to about 15% conversion at 1.3 torr. Consequently, the alkylation of 1-butene by these pentyl ions is roughly the same as the alkylation by the other ions.

The maximum concentration of heptyl ions is 1%, a value sufficiently below the concentration of hexyl ions in the propylene–isobutane mixture that one may say that there is a reaction in competition with alkylation of 1-butene by the propyl ions. Qualitatively, this is the same observation that was made for alkylation of 1-butene by propyl ions in the butane–propylene mixture.

There is no evidence for H⁻ transfer between $C_4H_9^+$ and $C_5H_{11}^+$ or $C_8H_{17}^+$ and 1-C_4H_8.

1-Pentene. The major ions in this mixture of isobutane and 6.4% 1-pentene at 1.2 torr are $C_9H_{19}^+$ (31%), $C_4H_9^+$ (20%), $C_5H_{11}^+$ (14%), $C_6H_{13}^+$ (6%), $C_{10}H_{21}^+$ (6%), and $C_{11}H_{23}^+$ (0.8%). The reactions appear to be much the same as those mentioned previously for the 1-pentene–butane mixture; however, there are appreciable differences in the relative concentrations of the ions, particularly $C_5H_{11}^+$ and $C_9H_{19}^+$. These differences have been discussed before to distinguish between *t*-butyl and *sec*-butyl ions.[7] Since simple proton transfer from the *t*-butyl ions to give *sec*-pentyl ions is endothermic and should not be a favorable process, one expects an appreciable rearrangement in this intermediate complex. It would be valuable to study the reactions with deuterated butyl ions to try to observe further differences in these $C_9H_{19}^{+*}$ complexes from the deuterium distribution in the resultant pentyl ions.

The low concentration of octyl ions, 1% of the total ionization, agrees with the previous observations and supports the contention from the butane mixtures that propyl ions alkylate 1-pentene less readily than they alkylate propylene.

The relative concentrations of $C_{10}H_{21}^+$ and $C_{11}H_{23}^+$ correspond to about 30 and 10% conversion of the pentyl and hexyl ions at 1.2 torr. The conversion of $C_4H_9^+$ to $C_9H_{19}^+$ is about 35% at 1.2 torr. The ratio of hexyl to pentyl ions is about one-third and the ratio ($C_{11}H_{23}^+$)/($C_{10}H_{21}^+$) is about one-tenth so that alkylation by the hexyl ions is perhaps one-third of the alkylation by pentyl ions. All of the alkylation reactions are proceeding at roughly the same rate (a difference of less than a factor of 10).

There is no evidence at high pressures for H⁻ transfer reactions between the higher alkyl ions and C_5H_{10}.

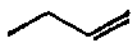
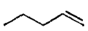
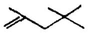
***t*-2-Butene.** As indicated in Figures 3 and 4 there is appreciably less reaction of butyl ions with 2-butene than with 1-butene. At 1.2 torr the concentrations of the major ions are $C_4H_9^+$ (75%), $C_5H_{11}^+$ (2.5%), $C_8H_{15}^+$ (1.6%), and $C_8H_{17}^+$ (5.7%). Qualitatively the reactions appear to be the same as those for butane and 2-butene; however, in addition to the lower concentration of $C_5H_{11}^+$, 2.5% contrasted with 22%, the ratio ($C_8H_{15}^+$)/($C_5H_{11}^+$) is about 0.6 rather than 0.2. The net rate of disappearance of butyl ions is about 0.4 × 10^{10} cc/molecule sec. All of these observations indicate that this $C_8H_{17}^{+*}$ complex is different from the complex formed from *t*-$C_4H_9^+$ and 1-C_4H_8 or *sec*-$C_4H_9^+$ and 2-C_4H_8.

In agreement with the observations made on the mixture of 2-butene and butane, there is very little $C_7H_{15}^+$ (<0.2%); hence, alkylation of 2-butene by propyl ions is slow compared with the alkylation of propylene by propyl ions. No evidence was found for H⁻ transfer reactions of $C_8H_{17}^+$ or $C_5H_{11}^+$ with 2-C_4H_8, and the pentyl ions did not react to give nonyl ions.

Isobutylene. Essentially the only product ions from the reaction of *t*-butyl ions with isobutylene are the octyl ions formed as 13% of the total ionization at 1.3 torr. Essentially no $C_5H_{11}^+$ is formed from the butyl ions (<0.5%) for pressures above 0.5 torr. A small amount of $C_5H_{11}^+$ is formed by a second-order process (1.5%) at 0.05 torr in this mixture and it reacts rapidly, but not to give nonyl ions. No H⁻ transfer of $C_8H_{17}^+$ with *i*-C_4H_8 to give $C_4H_7^+$ appears to be occurring. Alkylation with propyl ions is trivial since the relative concentration of $C_7H_{15}^+$ is never greater than 0.6% of the total ionization. The rate constant for the disappearance of $C_4H_9^+$ is about 0.7 × 10^{-10} cc/molecule sec in this mixture.

2,4,4-Trimethylpentene. Figure 5 shows the relative concentrations of three of the major ions in this mixture of 3.5% 2,4,4-trimethylpentene and isobutane. The

Table I. Major Reactions of Butyl Ions with Olefins

Olefin	sec-$C_4H_9^+$ k, 10^{-10} cc/molecule sec	sec-$C_4H_9^+$ Products at 1 torr	t-$C_4H_9^+$ k, 10^{-10} cc/molecule sec	t-$C_4H_9^+$ Products at 1 torr
	3.2	$C_7H_{15}^+$	1.4	$C_7H_{15}^+$
	5.7	$(C_5H_{11}^+)/(C_8H_{17}^+) \simeq 1$	2.7	$(C_5H_{11}^+)/(C_8H_{17}^+) \simeq 0.5$
	3	$(C_5H_{11}^+)/(C_8H_{17}^+) \simeq 3$	0.4	$(C_5H_{11}^+)/(C_8H_{17}^+) \simeq 0.5$
	0.5	$(C_5H_{11}^+)/(C_8H_{17}^+) \simeq 0.5$	0.7	$(C_5H_{11}^+)/(C_8H_{17}^+) \simeq 0.04$
	10	$(C_5H_{11}^+)/(C_6H_{13}^+)/(C_9H_{19}^+) \simeq 1:0.3:0.5$	7	$(C_5H_{11}^+)/(C_6H_{13}^+)/(C_9H_{19}^+) \simeq 1:0.3:2.0$
	. . .	. . .	13	$C_8H_{17}^+$

predominant reaction of the *t*-butyl ion is proton transfer to give the octyl ion. Essentially no $C_{12}H_{25}^+$ or $C_{16}H_{33}^+$ ions are formed since the ion currents at *m/e* 169 and 225 are never greater than 0.2% of the total ionization. In Figure 5 it appears that $C_4H_9^+$ is a second-order ion which reacts further and that $C_8H_{17}^+$ is a third-order ion. A plot of log $(I_{57}/\Sigma I_t)$ *vs.* *P* is not a particularly good straight line, but a rate constant of about 13 × 10^{-10} cc/molecule sec may be estimated. The curves for both $C_8H_{17}^+$ and $C_4H_9^+$ appear to be reaching constant values, and this observation suggest a possible approach to a pseudo-equilibrium between these two ions.

Other alkyl ions are formed to small extents in this mixture, but their origins are obscure and they will not be discussed.

Conclusions

The rate constants for reactions of both *sec*-butyl and *t*-butyl ions with the olefins increase with increasing molecular weight of the olefins. No reliable estimate can be given about the variation, however, and generalizations from these data are very uncertain because of the appreciable variation in rate constants with the structure of the isomeric olefins. Table I summarizes these results. Differences are observed for the products among all of the reactions of the isomeric butenes. It is apparent that even though strong complexes involving new C–C bonds are formed in all of these systems, the $C_8H_{17}^{+*}$ complexes do not rearrange to give identical structures.

These differences in concentrations of the octyl ions in these mixtures are measures of the stabilities and lifetimes of the intermediate complexes. In Figures 2 and 4 the octyl ions are written without rearrangement to the most stable species by H and CH_3 shifts. The rates of these isomerization reactions may be sufficiently rapid to occur within the microsecond or less times of these experiments. The explanations for these differences in octyl ion concentrations are not obvious, but some information about the processes may be gleaned.

The difference between products of *sec*-butyl ions with 1- and 2-butene indicates that the attack is not at the same carbon atom in both cases. Without appreciable rearrangements it is very difficult to see how $C_5H_{11}^+$ ions are formed in either case. Since the relative concentrations of the $C_5H_{11}^+$ ions are similar for these two compounds, it is tempting to say that the more highly branched octyl ion from addition to 2-butene dissociates more readily into butyl ions and butene than does the ion from addition of butyl ions to 1-butene. It is also noteworthy that the pentyl ions and *t*-butyl ions both add less readily to this internal olefin than to 1-butene.

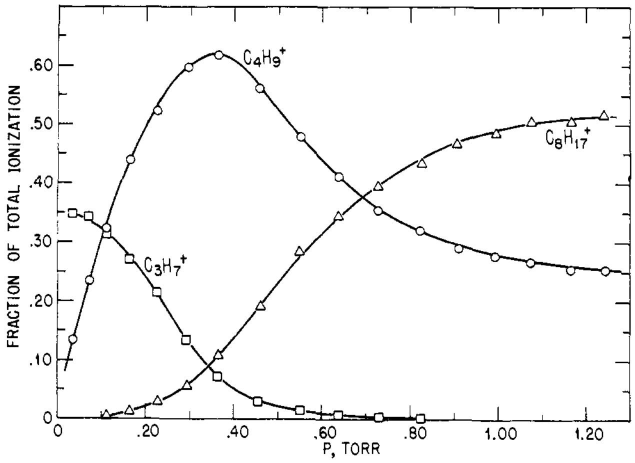


Figure 5. Major product ions in *i*-C_4H_{10} + 3.5% 2,4,4-trimethylpentene.

There is consistently more alkylation than condensation for *t*-butyl ions with the butenes and 1-pentene, but this observation is not true for *sec*-butyl ions. The reaction of *t*-butyl ions with isobutylene is essentially a clean three-body alkylation reaction in contrast with the reactions for the other combinations of butyl ions and butenes. The rates of reaction of *t*-butyl ions with these compounds are smaller than the rates of reaction of *sec*-butyl ions.

The formation of large amounts of $C_8H_{17}^+$ ions in the mixture of isobutene and 2,4,4-trimethylpentene is an indication that highly branched alkyl ions are stable under mass spectrometric conditions. In the chemical ionization mass spectra of paraffins it was observed earlier that $(MW - 1)^+$ ions were much less abundant for highly branched paraffins than for normal paraffins.[8] However, in those experiments the branched alkyl ions were formed by proton transfer of CH_5^+ or hydride transfer to $C_2H_5^+$. Both of these reactions are exothermic (25–30 kcal/mole to give simple secondary ions), but the proton transfer reaction from *t*-butyl ion to 2,4,4-trimethylpentene must be essentially thermoneutral. The β-fission reactions discussed for the branched alkyl ions in the chemical ionization spectra[8] may certainly be expected for this 2-2,4,4-trimethylpentyl ion. Apparently, then, the stabilities of these highly branched alkyl ions are extremely sensitive to their energy content.

Previously it has been observed that the electron impact mass spectra of paraffins at low pressures show appreciable temperature coefficients.[9] In particular, the $C_nH_{2n+2}^+$ ions from alkanes become relatively much more abundant at lower temperatures than at the high temperatures conventionally used for electron impact mass spectra of high molecular weight materials. Also for several branched hydrocarbons, the relative abundances of high molecular weight alkyl fragment ions $C_nH_{2n+1}^+$, increases with decreasing temperature. Similar temperature effects have been observed in the chemical ionization mass spectra of paraffins with methane as the reactant gas.[8] In these experiments it was noted that the $(MW - 1)^+$ alkyl ions increased in relative abundance with decreasing temperatures. All of these experiments indicate that the stabilities of branched alkyl ions are very sensitive functions of their energies of formation.

Figures 1 and 3 show butyl ion concentrations as functions of pressure for mixtures of butane and 2,2,4-trimethylpentane and isobutane and 2,2,4-trimethylpentane. These mixtures have been discussed briefly before[7] and were not discussed separately here. It is worth noting, however, that H^- transfer reactions for the butyl ions to this paraffin are slower than the proton transfer and alkylation reactions with some of the olefins. The rate constant for H^- transfer between *sec*-butyl ions and 2,2,4-trimethylpentane is roughly 1×10^{-10} cc/molecule sec, and the rate constant for H^- transfer between *t*-butyl ions and 2,2,4-trimethylpentane is about 1×10^{-11} cc/molecule sec. This surprisingly small value may be compared with the value of 1×10^{-9} cc/molecule sec for proton transfer from *t*-butyl ions to 2,4,4-trimethylpentene. Both reactions should be essentially thermoneutral. The failure to observe appreciable concentrations of octyl ions in the mixtures of isobutane and 2,2,4-trimethylpentane cannot be the result of subsequent decompositions of these octyl ions, since they should be formed with nearly the same energy by H^- transfer from 2,2,4-trimethylpentane and H^+ transfer to 2,4,4-trimethylpentene.

The failure to observe products from alkylation of the butenes and 1-pentene with propyl ions shows that there must be a rapid reaction for the decomposition of the intermediate complex. From the large amount of pentyl ions formed from the butyl ions in the butane–1-pentene mixture, it would seem that this reaction is proton transfer with the butenes, as well. The *t*-butyl ions from isobutane readily transferred protons to 2,4,4-trimethylpentene. No evidence was provided for proton transfer from *sec*-butyl ions to propylene. Perhaps, then, rapid proton transfer occurs from a lower molecular weight alkyl ion to give a higher molecular weight alkyl ion of the same type, but not the reverse.

Since the heats of formation of the methallyl ions, $C_4H_7^+$, from all of the butenes are about 203 kcal/mole, hydride transfer to any secondary carbonium ion should be exothermic.[10] This observation should hold as long as the heats of formation of the $C_nH_{2n-1}^+$ and $C_nH_{2n+1}^+$ ions differ by less than the heats of hydrogenation of the olefins, 25–30 kcal/mole. H^- transfer to *t*-butyl ions and by inference to other tertiary carbonium ions is endothermic by a few kcalories/mole. The present experiments would not show slow H^- transfer reactions because of the complexities of the kinetics, but H^- transfer between any of these olefins and alkyl ions is minor with respect to proton transfer and alkylation. The reactions of these alkyl ions with the olefins appear to be predominantly electrophilic attack at the double bond.

$$C_4H_9^+ + C_4H_8 \longrightarrow C_4H_7^+ + C_4H_{10} \qquad (10)$$

There has been some recent work on ion–molecule reactions in the butenes at pressures as high as 0.5 torr[11] which may be compared somewhat with these experiments. Several primary ions were present for each compound so the spectra were very complex at high pressures. For isobutylene the dominant product was $C_4H_9^+$ which then reacted to give predominantly $C_8H_{17}^+$ which then gave $C_{12}H_{25}^+$ and $C_{16}H_{33}^+$ ions. Much smaller amounts of butyl ions were formed in the other butenes and these also apparently gave $C_8H_{17}^+$ ions. In all cases, however, the reactions of the ions at high pressures predominantly involved that addition of C_4H_8 to the ions.

Gaseous ionic alkylation has recently been observed to produce octanes or polyisobutylene[12–14] in precisely the manner indicated by the ion–molecule studies. In the experiments of Viswanathan and Kevan[14] more octenes than octanes were produced. The present experiments show that H^- transfer from isobutylene is slow and suggest that proton transfer to isobutylene would be the preferred reaction for the octyl ions.

The present experiments and more definitely those of Aquilanti, *et al.*,[11] show that ionic polymerization may give higher molecular weight species between octanes and polyisobutylene. Since the stabilities and lifetimes of the excited octyl intermediates in the polymerization of isobutylene depend critically on their energy content, it seems likely that the higher molecular weight ions are more likely to decompose at higher temperatures to give products other than those formed by the simple addition of isobutylene units.

With regard to the elementary steps of alkylation, several similarities are noted between gaseous and solution processes. The rapid H^- transfer initiation reactions for alkylation with isobutane have been observed mass spectrometrically. The three-body alkylation of olefins by *t*-butyl ions has also been observed. Differences were also noted in the alkylation rates with different olefins. There are suggestions from these experiments of hydride transfer reactions from isobutane to octyl ions as one of the chain steps. Slow hydride transfer from 2,2,4-trimethylpentane to *t*-butyl ions and rapid proton transfer from *t*-butyl ions to 2,4,4-trimethylpentene were observed as possible chain transfer reactions. H^- transfer from olefins to

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(9) See J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, pp 429–430.

(10) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Table 45.

(11) V. Aquilanti, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *Trans. Faraday Soc.*, **63**, 926 (1967).

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(14) N. S. Viswanathan and L. Kevan, *ibid.*, **89**, 2842 (1967).

t-butyl ions or octyl ions appears to be slow. The present experiments show that gaseous ionic alkylation may be studied in detail by high-pressure mass spectrometry and suggest further studies to determine more precise information about the individual steps in the processes.

The Anodic Oxidation of Organic Compounds. III. The Effect of Electrolyte on Electrochemical Methoxylation and Dimerization of N,N-Dimethylaniline

N. L. Weinberg and T. B. Reddy

Contribution from the Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904.

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Abstract: Electrode kinetic data for N,N-dimethylaniline (DMA) oxidation in methanol employing potassium hydroxide or ammonium nitrate as electrolytes show the reaction order to be fractional with respect to DMA due to adsorption. Furthermore, one electron is transferred in the rate-controlling step for each of these systems as determined from Tafel plots. Mechanisms are proposed which depict the importance of adsorption of DMA in the formation of N-methoxymethyl-N-methylaniline from the DMA–potassium hydroxide–methanol system and of N,N,N′,N′-tetramethylbenzidine (TMB) from the DMA–ammonium nitrate–methanol medium.

The anodic oxidation of tertiary amines in methanol has been shown[1] to give products with structures indicating the importance of adsorption of the electroactive species on the anode. In one example, N,N-dimethylaniline (DMA) was methoxylated, affording N-methoxymethyl-N-methylaniline (I). On further oxidation, N,N-bis(methoxymethyl)aniline (II) was obtained. No N-dimethoxymethyl-N-methylaniline (III) was detected.

$C_6H_5N(CH_3)CH_2OCH_3$
I

$C_6H_5N(CH_2OCH_3)_2$
II

$C_6H_5N(CH_3)CH(OCH_3)_2$
III

In contrast to the electrochemical oxidation of DMA in methanol are the results reported for other solvents. Electrochemical kinetic studies of DMA oxidation in aqueous acid[2–7] were initially interpreted in terms of a two-electron transfer forming a dication with a reaction order for DMA of unity.[8,9] Since the establishment of new diagnostic criteria for cyclic voltammetric studies of charge-transfer processes with coupled chemical reactions, Adams and co-workers[5] have reinterpreted their work in aqueous acid in terms of a one-electron oxidation followed by a fast chemical reaction. In anhydrous acetic acid,[10] the reaction order is two for DMA with one electron involved in the rate-controlling step.

Similar studies have now been carried out for DMA in methanol containing potassium hydroxide and ammonium nitrate electrolyte. Under conditions of controlled potential electrolysis[11] at 1.20 v *vs.* the saturated calomel electrode (sce), the oxidation of DMA in the potassium hydroxide–methanol solution gave the methoxylated product I. Changing the electrolyte to ammonium nitrate, however, provided TMB as the mononitrate salt. Thus the effect of ammonium nitrate on the electrochemical kinetics of DMA oxidation has also been included here.

Current–voltage curves (Figure 1) for the background oxidation of the solvent demonstrated that the more acidic ammonium nitrate–methanol system was oxidized about 0.5 v more anodic than the corresponding potassium hydroxide–methanol solution. On addition of DMA, oxidation occurred at a lower potential, signifying that solvent or electrolyte oxidation was not involved.

Tafel plots of log current density against potential are shown for the low current density regions in Figure 2. The slopes of the linear regions were each 117 mv/decade, implying that one electron was transferred in the rate-determining step, assuming a symmetry factor of 0.51.

The log–log plots of current against concentration for DMA oxidation in solutions 0.5 *M* in each electrolyte are shown in Figure 3. Determination of the reaction order from the slopes of the linear regions gave values of 0.51 and 0.64 for the potassium hydroxide and

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(8) The reaction order may be obtained from the slope of the log–log plot of current against concentration at constant potential, while the slope of the log current density–potential curve (Tafel plot) gives the value $\beta zF/2.30RT$ where R is the gas constant, T is the absolute temperature, β is the symmetry factor (usually 0.5), z is the number of electrons transferred up to and including the rate-determining step, and F is the Faraday. Further details may be found in ref 9.

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