Swinehart, Rogers, and Taube[2b] measured rate constants by isotope dilution experiments for methanol solutions containing 0.9 mole of $H_2O$ per 1 mole of $Mg(ClO_4)_2$. Their results are $1.12 \times 10^{-3}$ sec$^{-1}$ at $-96.9°$ and $1.87 \times 10^{-2}$ sec$^{-1}$ at $-82.5°$. From these two values they calculated the activation parameters, $\Delta H^{\ddagger} = 12.5 \pm 2.0$ kcal mole$^{-1}$ and $\Delta S^{\ddagger} = 4 \pm 4$ eu. When our results are extrapolated to $-82.5°$, $k = 3.5 \times 10^{-4}$ sec$^{-1}$ is obtained. This is about $^1/_{50}$th of the quoted results of Swinehart, Rogers, and Taube. This discrepancy is presumably due to the acceleration of the exchange by water, as already noted by these authors, and their rates and activation parameters are probably predominantly for the monohydrated complex. The predominance of the monohydrate when water is present is seen in Figure 3. This figure also indicates that at $-44°$ the monohydrate still exchanges relatively slowly, and that at this temperature the ratio of the exchange rates for the hexamethanolate and the monohydrate is larger than the ratio 1/50 quoted above for $-82.5°$. An order of magnitude calculation shows that a consistent picture is obtained if the activation energy of 12.5 found by Swinehart, Rogers, and Taube is roughly that for the monohydrate, while the higher figure of 16.7 of the present work is that for the hexamethanolate.

The clean linearity of the Arrhenius plot extending to the higher temperature also sheds some light on the solvation number at these temperatures. If there were any drastic change in the structure of the solvation shell, say a change in solvation number, one would expect it to show up in the behavior of the rate constant with the temperature. Absence of any such obvious effect in the Arrhenius plot indirectly argues against such a drastic change. Also, in view of the relatively low rate of exchange observed, it appears to be well justified to conclude that the first solvation shell for $Mg^{2+}$ exists as a well-defined entity and contains six methanol molecules in the temperature range studied.

The pronounced effect of pH on the nmr signals, which we have not been able to study closely because of the difficulties stated earlier, prohibits the extrapolation of the observed rates to neutral or basic media. Fast proton exchange in basic solution is not at all unexpected, but the possibility of a base-catalyzed ligand exchange is also not ruled out and requires further investigation.

**Acknowledgments.** We thank Dr. M. Cocivera for making his computer program available and for many discussions. The high performance of the nmr spectrometer used in this work is largely due to the contributions of Mr. R. C. Hewitt.

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# Reactions of Isomeric Ions[1]

**M. S. B. Munson**

*Contribution from Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas.* *Received November 12, 1966*

**Abstract:** It is shown in this paper that the butyl ions produced by ionic reactions in *n*-butane react differently from the butyl ions produced by ionic reactions in isobutane with propylene, 2,2,4-trimethylpentane, and 1-pentene. The ions which are formed in the two gases do not have the same structure and do not rearrange in times short compared with a microsecond.

In a previous study on the kinetics of ionic reactions in hydrocarbons, it was reported for *n*-butane and isobutane that the major reactions were hydride-transfer reactions which produced $C_4H_9^+$ as the dominant ions for both compounds.[2] It was not possible then to determine whether the two butyl ions were the same or different, but, intuitively, one would think that they were initially different, even if *sec*-$C_4H_9^+$ rearranged to *t*-$C_4H_9^+$ during the time of the experiments ($10^{-6}$ sec). It is difficult to determine directly the structures of ions produced by electron impact, although indirectly it has been possible to establish that isomeric ions may have different heats of formation[3a] and it has also been possible to observe differences in ionization potential for isomeric radicals.[3b] It is the purpose of this paper to show that it is possible to observe by high-pressure mass spectrometry different reactivities for isomeric ions and hence differentiate between structures.

Ausloos and co-workers[4] have performed radiation studies on hydrocarbon systems in which they have interpreted some of their results in terms of several ion-molecule reactions. From experiments with deuterium-labeled compounds, information was derived concerning the reactivities of different positions for attack by several ions and the structures of these ions. The ionic intermediates, however, are not directly observable in these experiments, although analysis of the final products gives unambiguous determination of the labeled positions. For example, the formation of $CD_3CDHCD_3$ in mixtures of $(CH_3)_3CH$ with $(CD_3)_3CD$

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[1] Presented in part at the Southwest Regional American Chemical Society Meeting, Albuquerque, N. M.

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

[3] (a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957; (b) F. P. Lossing and J. B. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

[4] (a) R. P. Borkowski and P. J. Ausloos, *J. Chem. Phys.*, **38**, 36 (1963); (b) R. P. Borkowski and P. J. Ausloos, *ibid.*, **39**, 818 (1963); (c) P. Ausloos and S. G. Lias, *Discussions Faraday Soc.*, **39**, 36 (1965); (d) S. G. Lias and P. Ausloos, *J. Chem. Phys.*, **43**, 2748 (1965); (e) P. Ausloos, S. G. Lias, and A. A. Scala, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, pp 264–277.

was interpreted as a hydride-transfer reaction of *sec*-$C_3H_7^+$.[4a] Only very recently have mass spectrometric experiments been performed by Sieck and Futrell[5] which show differences in reactivities for $C_3H_6^+$ ions from two different compounds.

## Experimental Section

**Instrumental.** The instrument in its present form has been adequately described.[6] The *n*-butane, isobutane, propylene, and 2,2,4-trimethylpentane which were used in these experiments were Phillips Research Grade chemicals, and the 1-pentene was a fresh API sample. The compounds were used without further purification. The mixtures were prepared volumetrically and allowed to stand overnight to ensure complete mixing. The experiments were performed by maintaining a given pressure within the source of the mass spectrometer and scanning the mass spectrum over the range of interest and then increasing the pressure and redetermining the mass spectrum. The residence time of the ions is assumed to remain substantially constant over the entire pressure range.[7] This method of pressure variation will produce essentially the same results as those produced by changing the residence time of the ions. In these experiments the electron energy was approximately 800 v. This high value of the electron energy was used because it provided a higher ion current at source pressures of the order of 1 torr of butane than the lower electron energy which we have used previously.[2,6,7] It seems reasonable that this higher ion current is due primarily to the greater penetration into the source by the higher energy electrons because of the lower ionization cross section at the higher energy and to additional multiple ionization from the higher energy electrons. It is probable that with 800-v electrons ions are formed more nearly uniformly across the width of the source, and with the lower energy electrons the ions are formed predominantly very near the electron entrance slit where they cannot leave the source as readily. The source temperature was maintained at 200 ± 10° and the repeller was kept at 5 v which corresponds to a field strength of 12.5 v/cm.

## Data and Results

In *n*-butane, $C_4H_9^+$ (which will be assumed to have a secondary structure in the discussion in the remainder of the paper) is formed by predominantly second-order processes and has an essentially constant value of 76% of the total ionization from 0.6 to 1.4 torr (the highest pressure of these experiments). Only 1–2% of the $C_4H_9^+$ is formed from direct ionization by the electrons. The primary ions react with *n*-butane with rate constants of the order of $10^{-10}$ to $10^{-9}$ cc/molecule sec. As we have noted previously, $C_3H_7^+$ is formed by a reaction of some of the primary ions with *n*-$C_4H_{10}$ by what is at least formally a methide abstraction reaction.[2] In addition, there is evidence that $C_3H_6^+$ and $C_3H_5^+$ are produced by ionic reactions, but all three of these ions react with *n*-butane with rate constants of the order of $10^{-10}$ to $10^{-9}$ cc/molecule sec.

For isobutane, *t*-$C_4H_9^+$ is formed by hydride-transfer reactions and attains an essentially constant value of 92% of the ionization between 0.6 and 1.3 torr (the highest pressure of these experiments). Only 1–2% of the $C_4H_9^+$ is formed by direct ionization. As was the case with *n*-butane, $C_3H_7^+$ is definitely formed and there is some evidence for the formation of $C_3H_5^+$ and $C_3H_6^+$, but these and the other primary ions react with isobutane with rate constants of the order of $10^{-10}$ to $10^{-9}$ cc/molecule sec.

The rate constants for the reactions of the primary ions with *n*-butane and isobutane are the same magnitude as have been observed for most gaseous ion-molecule reactions, and they indicate roughly a 1:1 correspondence between collision and reaction. On the other hand, from the constancy of the relative concentrations of the two butyl ions above 0.6 torr, it is possible to estimate that the rate constants for reaction of these two ions with either *n*-butane or isobutane are less than $10^{-12}$ cc/molecule sec., except for the possible hydride-exchange reaction

$$C_4H_9^+ + C_4H_{10} \longrightarrow C_4H_{10} + C_4H_9^+ \qquad (1)$$

Two of the most abundant primary ions in both *n*-butane and isobutane are $C_2H_3^+$ and $C_3H_7^+$. In addition $C_3H_7^+$ is produced by reaction; so it is perhaps sufficient to represent the formation of butyl ions as coming from hydride-transfer reactions of these two ions.

$$sec\text{-}C_3H_7^+ + n\text{-}C_4H_{10} \longrightarrow sec\text{-}C_4H_9^+ + C_3H_8 \qquad \Delta H = 0 \text{ kcal/mole} \qquad (2)$$

$$C_2H_3^+ + n\text{-}C_4H_{10} \longrightarrow sec\text{-}C_4H_9^+ + C_2H_4 \qquad \Delta H = -51 \text{ kcal/mole} \qquad (3)$$

$$sec\text{-}C_3H_7^+ + i\text{-}C_4H_{10} \longrightarrow t\text{-}C_4H_9^+ + C_3H_8 \qquad \Delta H = -12 \text{ kcal/mole} \qquad (4)$$

$$C_2H_3^+ + i\text{-}C_4H_{10} \longrightarrow t\text{-}C_4H_9^+ + C_2H_4 \qquad \Delta H = -63 \text{ kcal/mole} \qquad (5)$$

The butyl ions may, therefore, be formed with either no excess energy or as high as a few tens kcal/mole.[8] However, reaction 1 could provide a path to degrade any excess energy in the butyl ions. If there is isomerization of *sec*-butyl ions to *t*-butyl ions after formation, then these ions should have about 14 kcal/mole of energy. If there is rearrangement during the lifetime of the collision complex, then there is essentially no difference in the energetics of the pairs of reactions.

Let us now consider the mixtures of the butanes with a few per cent of the other substances. The cross sections for ionization for propylene, pentene, and 2,2,4-trimethylpentane should be within approximately a factor of 2 of the ionization cross sections of the butanes.[9] Consequently, for the mixtures which were used in these experiments (6.4% propylene and 1-pentene and 2.5% 2,2,4-trimethylpentane) over 90% of the ionization by electron impact should be ionization of butane. In addition, since the rate constants are of the order of $10^{-10}$ to $10^{-9}$ cc/molecule sec for reactions of the primary ions with butane and for the reactions of the primary ions with the added compounds, all of these reactions will proceed in substantially the same manner in the mixtures as in the pure butanes. The fate of the butyl ions, however, is very different in the mixtures than it is in pure butane since the butyl ions do not react with the butanes but may react with the other components.

If the butyl ions are identical in *n*-butane and isobutane, then the rates of reaction of these ions with the added substances should be the same, and the product distribution should also be the same. If the rates of reaction and products are different, for example, between the butyl ions of *n*-butane with 1-pentene and

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(5) L. W. Sieck and J. H. Futrell, *J. Chem. Phys.*, **45**, 560 (1966).

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

(7) F. H. Field and M. S. B. Munson, *ibid.*, **87**, 3289 (1965).

(8) Heats for formation of these ions are obtained from a compilation in the process of preparation by J. L. Franklin: $\Delta H_f(sec\text{-}C_3H_7^+) = 195$, $\Delta H_f(sec\text{-}C_4H_9^+) = 190$, $\Delta H_f(t\text{-}C_4H_9^+) = 176$, $\Delta H_f(C_2H_3^+) = 283$ kcal/mole.

(9) F. W. Lampe, J. L. Franklin, and F. H. Field, *J. Am. Chem. Soc.*, **79**, 6129 (1957).

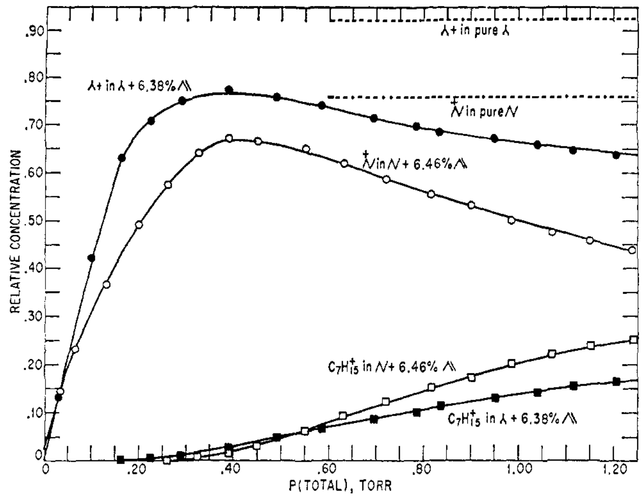


Figure 1. Butyl and heptyl ions in mixtures of butanes and propylene.

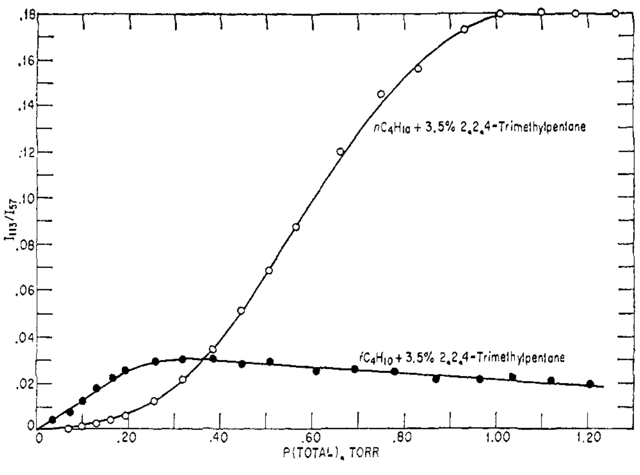
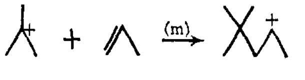


Figure 2. $(C_8H_{17}^+)/(C_4H_9^+)$ *vs.* *p*(total) for mixtures of butanes and 2,2,4-trimethylpentane.

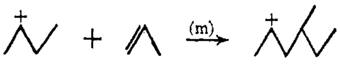
the butyl ions of isobutane with 1-pentene, then the ions are different in structure or energy content.

**Butanes + 6.4% Propylene.** Figure 1 shows the relative concentrations of butyl and heptyl ions in mixtures of 6.38% propylene in isobutane and 6.46% propylene in *n*-butane. The curves for the butyl ions are characteristic of second-order product ions which also react to give products. In the pressure region above 0.7 torr, there is about 1.4 times as much $C_7H_{15}^+$ in the mixture with *n*-butane as there is in the mixture with isobutane. If one considers the conversion of butyl ion to heptyl ion, $I_{99}/(I_{57} + I_{99})$, then the difference is even greater.

If the ionic addition proceeds in the gas phase as in solution, then



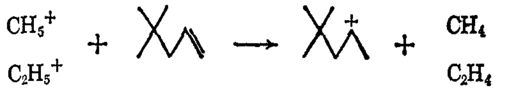
(6)



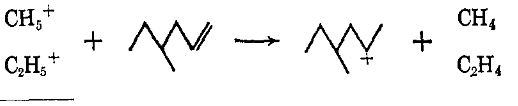
(7)

Although the correspondence with chemical ionization mass spectra of the paraffins is not exact, a rough parallelism may be expected for the stability of the ions. $(MW - 1)^+$ ions are much more abundant for monosubstituted paraffins (30–50% of the ionization) than for any of the 2,2-dimethylparaffins (5–10%).[10] Consequently, one might expect that the 4-methyl-2-hexyl ion would be more stable than the 4,4-dimethyl-2-pentyl ion and hence more abundant.

In addition, the chemical ionization mass spectra of 4,4-dimethyl-1-pentene and 4-methyl-1-hexene have been determined with methane as the reactant gas. For these two olefins the major reactions will be hydride transfer or proton transfer, which may or may not be dissociative. The proton transfer reactions are



(8)



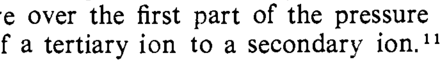
(9)

The two heptyl ions are formed with different energies in these reactions than in (6) or (7), and appreciable amounts of decomposition occur. However, the heptyl ions are 0.049 of the additive ionization for 4-methyl-1-hexene and only 0.030 for 4,4-dimethyl-1-pentene, in qualitative agreement with the previous observations on the relative abundances of the ions formed by addition of butyl ions to propylene.

If it were a matter of different energy content but the same structure, that is, if the *sec*-butyl ions were formed in *n*-butane and then rearranged to give *t*-butyl ions containing the excess energy, it seems more likely that these excited ions would give less addition product than the lower energy ions. Increasing the energy in the heptyl ions is hardly likely to increase their stability. The difference in reactivities of the two butyl ions suggests the differences in structure which have been assumed.

**Butanes + 3.5% 2,2,4-Trimethylpentane.** In these mixtures the concentration of the butyl ions is nearly the same as in the pure butanes; in isobutane the *t*-butyl ion increases to about 88% of the total ionization above 0.6 torr compared with 92% in pure isobutane, and the *sec*-butyl ion passes through a maximum of 72% and then gradually decreases to 68% of the total ionization at 1.2 torr compared with an essentially constant value of 76% above 0.6 torr in *n*-butane. There are very striking differences in the relative concentrations of the $C_8H_{17}^+$ ions: 2% with isobutane and 12% with *n*-butane. The ratios $I_{113}/I_{57}$ for these two mixtures are shown in Figure 2. The differences are sufficiently striking that one is again led to the conclusion that the reacting butyl ions in the two gases have different structures.

However, let us consider briefly some further consequences indicated by the two curves in Figure 2. If the reaction in the mixture of isobutane and 2,2,4-trimethylpentane is



(10)

then $C_8H_{17}^+$ should be initially proportional to the third power of the pressure, and $I_{113}/I_{57}$ should be linear in pressure over the first part of the pressure range, the ratio of a tertiary ion to a secondary ion.[11] Initially

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[10] F. H. Field, M. S. B. Munson, and D. A. Becker, ref 4e, p 167.

this rate is linear in pressure as one would expect. However, the gradual decrease indicates a more complicated mechanism. A reasonable explanation for these observations (compatible with, but not required by, the present data) is the occurrence of

(11)

The reaction should be essentially thermoneutral, and, if it occurs, it has a rate constant of the order of $10^{-11}$ cc/molecule sec, somewhat slower than the hydride ion abstraction reactions of the other ions with isobutane.

The higher pressure dependence for $I_{113}/I_{57}$ in the mixture of *n*-butane and 2,2,4-trimethylpentane is surprising and less easily understood. Perhaps stabilizing collisions are necessary to remove the excess energy of the octyl ion. However, isomerization of *sec*-butyl to *t*-butyl ions during the time of the experiments will not provide an explanation for the six times greater abundance of octyl ions in this mixture at 1 torr compared with the mixture of isobutane and 2,2,4-trimethylpentane.

**Butanes + 6.4% 1-Pentene.** Figure 3 shows plots of relative concentrations of butyl, pentyl, and nonyl ions in a mixture of 6.38% 1-$C_5H_{10}$ in *n*-butane. The curve for $C_5H_{11}^+$ is characteristic of an ion whose concentration depends on the third power of the pressure and is expected if the pentyl ion is formed by proton transfer from *sec*-$C_4H_9^+$ to 1-$C_5H_{10}$ (eq 11a). The higher kinetic order indicated for $C_9H_{19}^+$ is expected if a collision is necessary to stabilize the $(C_9H_{19}^+)^*$ intermediate complex formed by simple addition (eq 11b). Other product ions are formed in these mixtures, but they are not necessary for the present discussion and will not be considered here. The curves for these three ions in a mixture of 6.44% 1-$C_5H_{10}$ in isobutane are qualitatively the same but very different quantitatively. From plots of the logarithms of the relative concentrations of $C_4H_9^+$ as functions of pressure, it is possible to obtain approximate values for the rate constants for reaction of the two butyl ions with 1-pentene. The absolute accuracy is uncertain,[7] but the relative values should be reliable. The *sec*-$C_4H_9^+$ ion reacts approximately 1.5 times as fast as the *t*-$C_4H_9^+$ ions.

In addition, even more striking differences exist between the relative amounts of $C_5H_{11}^+$ and $C_9H_{19}^+$ produced in the two mixtures. At pressures above 0.5 torr only 55% as much $C_5H_{11}^+$ is produced in the isobutane–pentene mixture as is produced in the *n*-butane–pentene mixture. Also about 1.8 times as much $C_9H_{19}^+$ is produced in the isobutane–pentene mixture as is produced in the *n*-butane–pentene mixture. The magnitude of these differences supports the contention that the two ions have different structures.

The most plausible reactions in these mixtures are

$sec\text{-}C_4H_9^+ + 1\text{-}C_5H_{10} \longrightarrow$

$[C_9H_{19}^+]^* \rightarrow C_5H_{11}^+ + C_4H_8$ (10a)

$\rightarrow$ other possible ions

$\xrightarrow{(m)} C_9H_{19}^+$ (10b)

$t\text{-}C_4H_9^+ + 1\text{-}C_5H_{10} \longrightarrow$

$[C_9H_{19}^+]^* \rightarrow C_5H_{11}^+ + C_4H_8$ (11a)

$\rightarrow$ other possible ions

$\xrightarrow{(m)} C_9H_{19}^+$ (11b)

In addition, of course, other reactions forming $C_5H_{11}^+$ are possible, and all of the ions may react with 1-pentene. However, it is not necessary to have a complete knowledge of the reaction mechanism. Proton transfer (10a) is much more likely for the *sec*-butyl ion than for the *t*-butyl ion. This observation is not surprising since simple proton transfer to give the 2-pentyl ion is thermoneutral for the *sec*-butyl ion and 5–10 kcal/mole endothermic for the *t*-butyl ion. Indeed, because simple proton transfer to give the 2-pentyl ion is endothermic for the *t*-butyl ion, it seems reasonable that this reaction involves a very profound rearrangement of the $[C_9H_{19}^+]^*$ intermediate complex and that the ion formed is not the 2-pentyl ion.

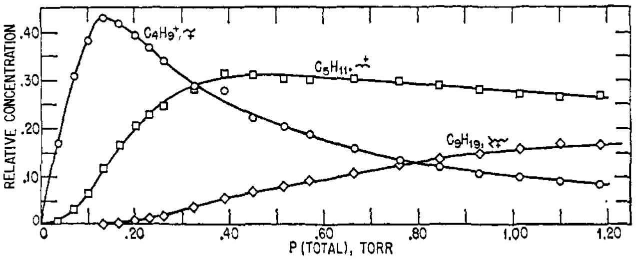

Figure 3. Relative concentrations of ions in *n*-butane + 6.38% 1-pentene.

## Summary

The three examples which have been presented in this discussion show that the butyl ions produced by ion–molecule reactions with *n*-butane and isobutane have different reactivities; that is, they react at different rates and give different product distributions with the same compounds. These differences in reactivity do not seem to be due to differences in energy for the same structure, but rather to different structures. On intuitive grounds, one would expect that the hydride-transfer reactions which form these ions would be fairly specific in removing hydrogens from the butanes, so that an initial difference in structure is expected. The present experiments suggest strongly that at 200° in the gas phase the *sec*-butyl ion does not isomerize to the *t*-butyl ion in times short compared to microseconds (the time of reaction of the ions within the source of the mass spectrometer).

The rapid isomerization of carbonium ions is well established, but the time scale is not. In recent studies on stable carbonium ions, it has been observed that in HF + $SbF_5$ at roughly room temperature, the primary, secondary, and tertiary alkyl fluorides ($C_3$, $C_4$, and $C_5$) gave the nmr spectra corresponding to the tertiary carbonium ion.[12] The times involved in these experiments, however, are much longer than the microseconds of the present work. On the other hand, experiments have been done which were interpreted as meaning that the lifetime of some primary alkyl ions in solution

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(11) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, **1**, 73 (1961).

(12) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(15–50% aqueous KOH) was $10^{-9}$ sec.[13] The present experiments are more direct than this earlier work and should be more meaningful. The present data agree with very recent observations from irradiation of hydrocarbon mixtures at pressures of approximately 40 torr which indicate that *sec*-$C_4H_9^+$ abstracts a hydride ion faster than it isomerizes to *t*-$C_4H_9^+$. Indeed, no evidence was reported for isomerization of *sec*-$C_4H_9^+$ to *t*-$C_4H_9^+$,[4e] and the experiments strongly corroborate each other.

**Acknowledgment.** The author is grateful to Drs. F. H. Field and J. L. Franklin for helpful discussions.

[13] P. S. Skell and R. J. Maxwell, *J. Am. Chem. Soc.*, **84**, 3963 (1962).

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# The Donnan Equilibrium in Cross-Linked Polystyrene Cation and Anion Exchangers[1]

**G. E. Boyd and K. Bunzl**

*Contribution from the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.*

*Received September 26, 1966*

**Abstract:** Techniques utilizing a "reference compound" and high specific activity $^{22}Na$, $^{36}Cl$, $^{35}S$, and $^{45}Ca$ were employed to determine the equilibrium water uptake and absorption of NaCl, $Na_2SO_4$, and $CaCl_2$ from dilute aqueous solutions by nominal 8% DVB cross-linked polystyrene-based cation and anion exchangers. Values of the molal distribution coefficients for electrolyte, $\lambda_D$, as small as 0.001 were measured, and the predictions of a general equation for the concentration dependence of $\lambda_D$, derived assuming a Donnan membrane equilibrium, were confirmed. The activity coefficients of electrolyte absorbed by the exchangers slowly increased as the external electrolyte concentration decreased below 0.1 *m*. It was concluded that the spherical ion exchangers employed were physically homogeneous to a high degree and that their absorption of strong electrolytes could be described quantitatively in terms of a Donnan equilibrium.

When two coexistent phases are subject to the restriction that one or several of the ionic constituents present in them cannot pass from one phase to another, a particular equilibrium, known as a Donnan equilibrium, is established. Usually the restriction is caused by a membrane which is permeable to solvent and to small ions but is impermeable to large ions; therefore, these equilibria are described as Donnan *membrane equilibria*. The presence of a membrane is not essential, however; in a gel or in an ion exchanger where there are structurally bound ions, the equilibria also are of the Donnan type.

The important aspects of the Donnan equilibrium with ion exchangers are that an unequal distribution of ions, an osmotic pressure difference, and a potential difference exist between the gel and external phases. In this paper, only the distribution of small ions and water will be considered for organic ion exchangers in which the charge density is high as with the cross-linked polystyrenesulfonate cation exchangers or polystyrene–quaternary ammonium type anion exchangers. Because of the high charge density, the Donnan equilibrium is nonideal and the thermodynamic treatment of Donnan and Guggenheim[2a] must be employed.

The equilibrium distribution of electrolytes between ion exchangers and dilute external aqueous solutions may be discussed in terms of the molal Donnan distribution coefficient, $\lambda_D$, defined by $\lambda_D = \bar{m}/m$, where $\bar{m}$ and $m$ are the electrolyte molalities in the ion exchanger and external solution phases, respectively. A general expression for $\lambda_D$ for a strong electrolyte dissociating into $\nu_c$ co-ions and $\nu_g$ counterions (or "gegenions") is[2b]

$$\lambda_D = (|z_c|m/\bar{m}_T)^{|z_c/z_g|}(\gamma_\pm/\bar{\gamma}_\pm)^{\nu/\nu_c}\exp(-\pi\bar{v}/RT) \quad (1)$$

where the total number of ions formed per mole of electrolyte, $\nu$, is given by $\nu = \nu_c + \nu_g$; $z_c$ and $z_g$ are the numbers of charges on the co-ion and counterions, respectively; $\bar{m}_T$ is the total molality of the ion-exchange phase given by $\bar{m}_T = (\bar{m}_R + |z_c|\bar{m}_c)$, where $\bar{m}_R$ is the molality of ion-exchange groups and $\bar{m}_c$ that of co-ions; $\gamma_\pm$ and $\bar{\gamma}_\pm$ are the mean molal activity coefficients of electrolyte in aqueous and exchanger phases, respectively; $\pi$ is the swelling pressure; and $\bar{v}$ is the partial molar volume of the electrolyte in the exchanger. The quantity $\exp(-\pi\bar{v}/RT)$ is approximately unity and constant and, henceforth, will be thus regarded.[3]

Writing eq 1 in the logarithmic form

$$\log \lambda_D = |z_c/z_g| \log (m/\bar{m}_T) - (\nu/\nu_c) \log (\gamma_\pm/\bar{\gamma}_\pm) + |z_c/z_g| \log |z_c| \quad (2)$$

The numerical value of the variation of log $\lambda_D$ with log $m$ will approach $|z_c/z_g|$, the absolute value of the ratio of the charge carried by the co-ion to that by the counterion, when the external electrolyte solution be-

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[2] (a) F. G. Donnan and E. A. Guggenheim, *Z. Physik. Chem.*, **A162**, 346 (1932). (b) This equation can be shown to be identical with equations (5–49) given by F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 142.

[3] Typical values for a nominal 8% divinylbenzene cross-linked polystyrenesulfonate exchanger invaded by an aqueous NaCl solution are: $\pi$ = 100 atm, $\bar{v}_{NaCl} \approx 25$ cc mole$^{-1}$, so that $\exp(-\pi\bar{v}_{NaCl}/RT) = 0.903$.