Figure 1. Dependence of ion exclusion
on the viscosity B coefficient.

preciable. McConnell, et al.,[6] tabulate values for the radii of hydrated cations *inside* silica gels derived from ion-exclusion measurements. If one interprets these "radii" as being some kind of a measure of ion exclusion, one might expect them to be related to the water-structure-altering capabilities of the cations as reflected in the B coefficient in the viscosity equation of Jones and Dole.[7] In Figure 1 the cationic radii given by McConnell, et al.,[6] are plotted vs. the cationic B coefficients at 25° given by Gurney.[8] Not only does the expected correlation obtain but the structure makers and structure breakers form two distinct curves, and the dependence of exclusion of the B coefficient is much greater in the latter case, as expected.

The phenomena discussed above probably play a role in the perturbation of the ionic constituents of sea water in marine sediments.[9]

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Argon Sensitized Radiolysis of Liquid Propane[1]

Sir: We wish to report evidence for very efficient liquid phase ionic reactions in the argon-sensitized radiolysis of liquid propane. The gas phase radiolysis of propane has received quite detailed study,[2-6] and the reactions of ionic species have been shown to be of major importance by careful isotopic experiments.[2a] Mass spectrometric studies of dissociative charge exchange of rare gas ions with propane have established the resulting gas phase ion distributions.[7] Rare gas sensitized radiolysis of propane has been interpreted on the basis of the charge-exchange distributions and has largely corroborated the importance of ionic reactions. The extensive gas phase data provide guidelines for assessing the importance of ionic reactions in the liquid. In analogy to Futrell's conclusion[2b] about the gas phase we may anticipate that a sensitive indicator of ionic processes will be ethane which is formed by hydride transfer.

In our laboratory we have succeeded in preparing solutions of argon and other rare gases with propane; these components are miscible over at least 0.5 to 0.1 mole fraction of propane. All samples were exposed to cobalt-60 γ irradiation at a dose rate of 0.602 ± 0.04 Mrad/hr to H_2O. A typical exposure time was 100 min. Analysis for all initial components and resulting products, except H_2, was accomplished by gas chromatography.

In Table I we compare the product yields from liquid propane at −130° with those from an argon–propane liquid mixture also at −130°. Results are given for oxygen scavenged and for unscavenged systems. It can be inferred from the nearly total disappearance of products greater than C_3 that O_2 is an efficient scavenger under these conditions. The yields are based on the total energy absorbed by the mixture. The exposure dose to the mixture and the pure liquid was the same, but because of energy transfer the "effective" dose to the propane in the mixture was about 9 times that for the pure liquid. Higher doses to the pure

(1) This work was supported by the Petroleum Research Fund.

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liquid show that the product distribution observed in the argon–propane mixtures is distinctive of the mixture rather than of a higher dose to propane.

Table I: Product Yields per 100 Ev (G) for Propane and Propane–Argon Liquid Mixtures at $-130°$, Scavenged and Unscavenged[a]

| | C$_3$H$_8$:Ar:O$_2$ | | | |
| | 1:0:0 | 1:0:0.04 | 1:13:0 | 1:13:0.10 |
	——1.17 Mrads——		——0.80 Mrad——	
CH$_4$	0.51	0.33	1.01	0.94
C$_2$H$_4$	0.48	0.35	0.35	0.31
C$_2$H$_6$	0.37	0.16	1.25	0.83
C$_2$H$_2$	0.07	0.04	0.10	0.08
C$_3$H$_6$	2.5	0.75	0.43	0.13
ΣC$_4$–C$_6$[b]	1.56	0.16	0.59	<0.02

[a] All data presented are averages of at least two separate samples. [b] Individual products were analyzed but are no pertinent to the main conclusions.

The G values of individual products in Table I show some striking characteristics resulting from energy transfer from argon to propane. Yields of ethane and methane have increased dramatically and selectively and are much higher than in pure propane. Thus, the large majority of propane decomposition arising from energy transfer produces ethane and methane. This selectivity is characteristic only of argon–propane mixtures. In xenon–propane mixtures energy transfer is indicated by the enhancement of *all* product yields; in fact, general enhancement is the usual result of studies of this kind.[8] The oxygen-scavenged argon–propane mixtures still exhibit large yields of methane and ethane. This suggests that these products arise *via* ionic or excited molecule reactions.

In the gas phase ethane is mainly produced by reaction 1 and methane is a product of reaction 2.[2] Other nonradical reaction possibilities exist which

$$C_2H_5^+ + C_3H_8 = C_2H_6 + C_3H_7^+ \tag{1}$$
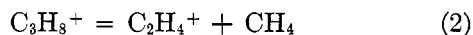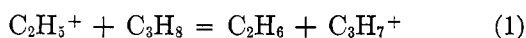
$$C_3H_8^+ = C_2H_4^+ + CH_4 \tag{2}$$

form methane and ethane $(C_2H_4^+ + C_3H_8 = C_2H_6 + C_3H_6^+)$, but (1) and (2) are the major reactions. The large and *selective* yields of ethane and methane that we observe in oxygen-scavenged argon–propane mixtures strongly indicate that reactions 1 and 2 occur *efficiently* in the liquid.

If the above conclusion is valid, the main mechanism of energy transfer must be charge exchange. The charge-exchange mass spectrum of propane with argon tells one the ion abundances observed in the gas phase. In the liquid much less fragmentation should occur,

and one would expect the charge-exchange fragmentation pattern for *liquid* propane with argon to be more like the gas phase pattern for propane with krypton or xenon than like the gas phase pattern for propane with argon. In the gas phase xenon charge-exchange spectrum, $C_2H_5^+$ and $C_2H_4^+$ comprise 87% of the ions. These two ions are just those we postulate for reactions 1 and 2. Further experiments with other rare gases and with isotopic labeling are in progress.

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Photosensitization in the Gas Phase with Hexafluorobenzene

Sir: For many years the sensitizer most often used in gas phase photochemical studies has been mercury or another volatile metal. In the past few years, however, some organic molecules have been increasingly utilized in this role. This shift may perhaps be traced to the advent of flash photolysis,[1] which has facilitated the identification of the triplet states of many organic molecules.

There are several advantages in the use of organic molecules as sensitizers, of which the most important is probably the wide range of energies available from such excited molecules. It is somewhat surprising, then, that only two organic molecules have been used in this role with any frequency. Thus, there is a considerable body of literature on the use of benzophenone in the liquid phase, as developed by Hammond and his collaborators.[2–4] Although benzene photosensitization has not been as widely accepted, it has been used successfully both in the gas phase[5,6] and in liquids.[7]

We have been interested for several years in the photolytic and photosensitized decompositions of small

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