Table VII. Solvent Shifts for a Series of 5,5-Dimethyl-1,3-dioxanes

Compound	ASIS,[a] Hz at 60 MHz CH$_3$	CH$_2$
2	10.22	10.09
3	7.08	5.35
4	6.56	6.05
5	6.36	5.52
6	5.30	

[a] Cyclopentane to toluene, at room temperature.

much because of "steric hindrance" of the oxygen heteroatoms,[58] but simply because there is a conformational change, a flattening of the dioxane ring upon introduction of an axial methyl group in position 2.[57,59]

Compounds **3**–**6** nicely exhibit the effect of molecular size discovered by Philipsborn and Winkler, a slight depression of the ASIS upon an increase of the molecular volume. We believe these to be the first polar solutes in which the effect of size is demonstrated simply by attachment of a variable hydrocarbon residue at a position distant from the polar sites. Notice in particular the intermediate position of the ASIS for molecule **4** between those for **3** and **5**: there are two dioxane rings in **4** and the moieties which would result in a formal sense from cleavage of the central cyclohexane ring along the middle would be in between **3** and **5**. The comparison of molecules **5** and **6** is also instructive: assuredly, the conformation of the dioxane ring is the same in both molecules, yet attachment of the bulky *tert*-butyl group modifies very significantly the ASIS perceived by the methyl protons situated at the other end of the molecule. It is for such reasons that we have maintained the solute's size constant throughout our study.

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(58) J. E. Anderson, *Tetrahedron Lett.*, 4713 (1965).

(59) (a) E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968); (b) unpublished ^{13}C work by Professor F. G. Riddell, University of Stirling, Scotland.

Ion Cyclotron Resonance Studies of Ionic Reactions in Ethane and of Hydrogen Exchange in D_2–C_2H_6 and H_2–C_2D_6 Mixtures[1]

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Abstract: Ionic reactions in pure gaseous ethane and in D_2–C_2H_6 and H_2–C_2D_6 mixtures have been investigated with the technique of ion cyclotron resonance spectroscopy. The observations on ethane lead to the establishment of mechanisms for the formation of $C_2H_4^+$, $C_2H_5^+$, C_3, and C_4 ions and the protonated species $C_2H_7^+$ and $C_3H_9^+$. The results resolve conflicting conclusions about these ions derived from previous high-pressure mass spectrometric experiments. The mechanisms of exchange of hydrogen isotopes during the ionic reactions that take place in D_2–C_2H_6 and H_2–C_2D_6 mixtures have also been determined. The modes observed serve as the basis for the sequences of reactions proposed to account for the nuclear-decay-induced and radiation-induced Wilzbach labeling of ethane by tritium.

The simple method devised by Wilzbach[2] for preparing tritium-labeled organic compounds has found widespread practical application in the tagging of complex molecules of biological and medical importance.[3] In this method a mixture of a compound and tritium is allowed to stand for some time, and the various tritiated products are then separated by radiogas chromatography. Interest in the fundamental hydrogen-exchange reactions taking place in this approach has resulted in several studies of the mechanisms of "Wilzbach labeling." Pratt and Wolfgang[4] have reported on an investigation of the kinetics of exchange in methane–T_2 mixtures, while Gant and Yang[5] have studied a number of gaseous mixtures of tritium with organic compounds, including ethane.[6] There was agreement between these pairs of workers that two modes of labeling were occurring: a decay-induced mechanism initiated by reaction of the T^3He^+ daughter formed directly from nuclear transformation of T_2 and a radiation-induced mechanism provoked by excitation and ionization of the compound and tritium by β particles released in the nuclear decays and by secondary electrons (self-radiolysis). Cacace, *et al.*,[7] have also investigated C_2H_6–T_2 mixtures under conditions where the former mode of tagging was predominant. In all these investigations the mechanisms proposed to account for the results were based on reactions of positively charged transient species.

The techniques of "high-pressure" mass spectrometry[8,9] and ion cyclotron resonance spectroscopy[10]

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) K. E. Wilzbach, *J. Amer. Chem. Soc.*, **79**, 1013 (1957); J. E. Wilzbach and P. Riesz, *J. Phys. Chem.*, **62**, 6 (1958); see also W. R. Ahrens, M. C. Sauer, and J. E. Willard, *J. Amer. Chem. Soc.*, **79**, 3284 (1957).

(3) "Proceedings of the 5th Annual Symposium on Advances in Tracer Technology," Vol. I, R. Rothchild, Ed., Plenum Press, New York, N. Y., 1963.

(4) T. H. Pratt and R. Wolfgang, *J. Amer. Chem. Soc.*, **83**, 10 (1961).

(5) P. L. Gant and K. Yang, *J. Chem. Phys.*, **32**, 1757 (1960); **31**, 1589 (1959); *J. Phys. Chem.*, **66**, 1619 (1962).

(6) P. L. Gant and K. Yang, *J. Chem. Phys.*, 30, 1108 (1959).

(7) F. Cacace, R. Cipollini, and G. Ciranni, *J. Amer. Chem. Soc.*, **90**, 1122 (1968).

(8) S. Wexler, *ibid.*, **85**, 272 (1963); *Exch. React. Proc. Symp., 1965*, 301 (1965).

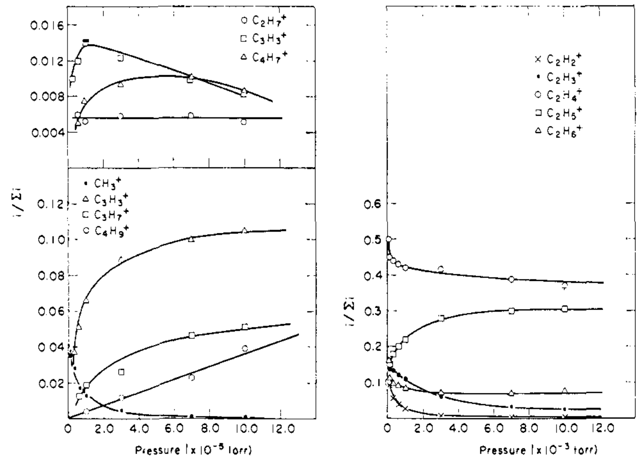

Figure 1. Relative abundances of positive ions in gaseous ethane at Syrotron cell pressures from 0 to 1.2 × 10^{-4} Torr.

(icr) have already been employed successfully in the mapping out of the complex pattern of concurrent and consecutive ion–molecule reactions taking place during isotopic exchange in methane–deuterium mixtures. As a consequence, we have extended the icr approach to the C_2H_6–D_2 and C_2D_6–H_2 systems in an effort to understand the ionic mechanisms responsible for the tritiation of ethane. (The D_2 and H_2 are stand-ins for T_2, and a beam of electrons simulates the radiation field created by the β particles and secondary electrons.) Furthermore, Aquilanti and Volpi[11] have described observations on ion–molecule reactions of H_3^+ and D_3^+ with ethane in a high-pressure mass spectrometer, and comparison of our results with theirs would be worthwhile.

Preliminary to investigation of isotopic exchange in ethane–hydrogen systems, we conducted icr experiments on ethane alone. In addition to serving as a basis for the exchange studies, they were performed in order to resolve a number of disagreements among several authors[12–17] on the ionic reactions taking place in gaseous C_2H_6. The high-pressure mass spectrometric technique was employed in these earlier efforts.

The ion cyclotron resonance studies reported in this paper were performed in a slightly modified[10] Varian Associates (Palo Alto, Calif.) Model V-5900 Syrotron.[18] Reagent ethane (99.98% Phillips Petroleum Co.) was further purified of methane and other impurities by alternate freezing plus pumping and volatilization. Fully deuterated ethane (99% minimum isotopic purity, Merck Sharp and Dohme Co.) and reagent hydrogen (99.9995%, Air Reduction Corp.) were used as received, while 99.5% deuterium (Air Products and Chemicals, Inc.) and 99.5% nitric oxide (Matheson Co.) were passed through glass coils at −195° in order to remove condensable impurities.

Results

Ethane. Presented in Figure 1 are the relative intensities, as a function of Syrotron cell pressure of ethane in the range from 0 to 1.2 × 10^{-4} Torr, of all positive ions except those of very low abundance. Typical experimental conditions for these single-resonance observations were the following: operating mode, pulse-drift modulation; observing rf power level, 80 mV/cm; electron beam current, 10 nA; electron energy, 75 V; trapping field, 220 mV/cm; analyzer drift field, 120 mV/cm; and source drift field, 320 mV/cm. The exponential decays of the fractional intensities as the pressure is increased indicate that the primary ions $C_2H_6^+$, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, and CH_3^+ are reactive, but $C_2H_5^+$ (nominally a primary moiety), $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_7^+$, and $C_4H_9^+$ behave like secondary or higher order species. The leveling off of the fractional yields of $C_2H_6^+$ and $C_2H_4^+$ at higher pressures suggests that they are also formed as products of ion–molecule reactions. $C_3H_3^+$ and possibly $C_4H_7^+$ appear to react with ethane, whereas the other polymeric ions seem to be unreactive in this pressure range. The behavior of $C_4H_9^+$ is suggestive of an ion of third kinetic order. The protonated ethane species $C_2H_7^+$ remains unchanged in fractional yield over the range of pressures. However, a log–log plot of the absolute intensity of $C_2H_7^+$ *vs.* pressure was approximately a straight line with a slope of two, an indication that this entity is the product of a reaction between a primary ion and an ethane molecule. The mass range up to 80 units was scanned in these experiments; above $C_4H_9^+$ only a very small yield of $C_5H_7^+$ was observed.

In order to establish unambiguously the reactant–product relationships in the many ion–molecule reactions that take place in irradiated ethane, we obtained the double-resonance spectra of all ions of significance. The experimental parameters for operating the Syrotron were the same as for the single-resonance studies, with the additional irradiating rf being set at a power level of 280 mV/cm. The data for ethane at a cell pressure of 3.0 × 10^{-5} Torr are collected together in Table I. In column 1 are listed the ions observed as all other ions were irradiated. In the next column are those species which when irradiated by the radiofrequency field resulted in a change in the single-resonance intensity of the respective observed ion. The double-resonance responses relative to single resonance in column 3 give an indication of the contributions of the irradiated reactants to the formation of the observed product species. The precursors of the product species so determined may be compared with those in column 4, which were arrived at in previous investigations by use of the high-pressure mass spectrometric technique. Column 5 gives the probable ionic reaction corresponding to each observed double resonance. The last column lists the calculated heats of reaction of the corresponding reactions of the previous column, based on the assumption that the ionic species are in their ground states. Since double-resonance signals are actually observed corresponding to endoergic reactions of several ground-

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(9) M. S. B. Munson, F. H. Field, and J. L. Franklin, *J. Amer. Chem. Soc.*, **85**, 3584 (1963).

(10) M. Inoue and S. Wexler, *ibid.*, **91**, 5730 (1969).

(11) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966); V. Aquilanti, A. Galli, and G. G. Volpi, *ibid.*, **47**, 831 (1967).

(12) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, **40**, 5 (1964).

(13) F. H. Field and F. W. Lampe, *J. Amer. Chem. Soc.*, **80**, 5587 (1958); **81**, 3242 (1959).

(14) A. Henglein and G. A. Muccini, *Z. Naturforsch. A*, **17**, 452 (1962).

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

(16) V. L. Talroze and E. L. Frankevich, *J. Amer. Chem. Soc.*, **80**, 2344 (1958).

(17) R. Fuchs, *Z. Naturforsch. A*, **16**, 1026 (1961).

(18) For a description of this instrument, see J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

Table I. Double-Resonance Spectra of Positive Ions in C_2H_6

Observed ion	Irradiated ion	Double-resonance signal intensity[a]	Precursors (earlier work)			Probable reactions	ΔH, kcal/mol
			Munson, *et al.*[b]	Volpi, *et al.*[c]	Fuchs[d]		
$C_2H_3^+$	$C_2H_4^+$	-2				$C_2H_4^+ + C_2H_6 \rightarrow C_2H_3^+ + C_2H_5 + H_2$	$+62$
	$C_2H_2^+$	-2				$C_2H_2^+ + C_2H_6 \rightarrow C_2H_3^+ + C_2H_5$	-2
$C_2H_4^+$	$C_2H_6^+$	$+3$	$C_2H_2^+$	CH_2^+		$C_2H_6^+ + C_2H_6 \rightarrow C_2H_4^+ + H_2 + C_2H_6$	$+8$
	$C_2H_2^+$	-1				$C_2H_2^+ + C_2H_6 \rightarrow C_2H_4^+ + C_2H_4$	-57
$C_2H_5^+$	$C_2H_4^+$	<-2	$(C_2H_6^+)^*$	$C_2H_6^+$		$C_2H_4^+ + C_2H_6 \rightarrow C_2H_5^+ + C_2H_5$	$+12$
	$C_2H_3^+$	-15	$C_2H_3^+$	$C_2H_4^+$		$C_2H_3^+ + C_2H_6 \rightarrow C_2H_5^+ + C_2H_4$	-17
	$C_2H_2^+$	<-2	$C_2H_2^+$	$C_2H_2^+$		$C_2H_2^+ + C_2H_6 \rightarrow C_2H_5^+ + C_2H_3$	-14
			CH_3^+	CH_3^+			
$C_2H_6^+$	$C_2H_5^+$	-3					$+72$
	$C_2H_4^+$	-6				Charge exchange	$+25$
	$C_2H_3^+$	-1					$+60$
	$C_2H_2^+$	$+1$					$+2$
$C_2H_7^+$	$C_2H_6^+$	-13	$(C_2H_6^+)^*$	$C_2H_6^+$		$(C_2H_6^+)^* + C_2H_6 \rightarrow C_2H_7^+ + C_2H_5$	$+\leq 30$
	$C_2H_5^+$	-3				$(C_2H_5^+)^* + C_2H_6 \rightarrow C_2H_7^+ + C_2H_4$	$+\leq 43$
	$C_2H_4^+$	-5				$(C_2H_4^+)^* + C_2H_6 \rightarrow C_2H_7^+ + C_2H_3$	$+\leq 60$
$C_3H_3^+$	$C_2H_2^+$	-13		C_2H^+	$C_2H_3^+$	$C_2H_2^+ + C_2H_6 \rightarrow C_3H_3^+ + CH_3 + H_2$	-8
	C_2H^+	-16			$C_2H_2^+$	$C_2H^+ + C_2H_6 \rightarrow C_3H_3^+ + CH_4$	-142
$C_3H_5^+$	$C_2H_4^+$	-2		$C_2H_3^+$	$C_2H_3^+$	$C_2H_4^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_3 + H_2$	$+17$
	$C_2H_3^+$	-31			$C_2H_2^+$	$C_2H_3^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_4$	-51
	$C_2H_2^+$	-17				$C_2H_2^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_3$	-47
	$C_3H_3^+$	-2				$C_3H_3^+ + C_2H_6 \rightarrow C_3H_5^+ + C_2H_4$	-6
$C_3H_6^+$	$C_2H_4^+$	-35				$C_2H_4^+ + C_2H_6 \rightarrow C_3H_6^+ + CH_4$	-22
	$C_2H_3^+$	-20				$C_2H_3^+ + C_2H_6 \rightarrow C_3H_6^+ + CH_3$	$+14$
	$C_2H_2^+$	-10				$C_2H_2^+ + C_2H_6 \rightarrow C_3H_6^+ + CH_2$	$+22$
$C_3H_7^+$	$C_3H_5^+$	-4	$C_2H_5^+$	$C_2H_4^+$	$C_2H_4^+$	$C_3H_5^+ + C_2H_6 \rightarrow C_3H_7^+ + C_2H_4$	$+7$
	$C_2H_5^+$	-3				$C_2H_5^+ + C_2H_6 \rightarrow C_3H_7^+ + CH_4$	-27
	$C_2H_4^+$	-33				$C_2H_4^+ + C_2H_6 \rightarrow C_3H_7^+ + CH_3$	-9
	$C_2H_3^+$	-5				$C_2H_3^+ + C_2H_6 \rightarrow C_3H_7^+ + CH_2$	$+31$
$C_3H_9^+$	$C_2H_6^+$	-34				$C_2H_6^+ + C_2H_6 \rightarrow C_3H_9^+ + CH_3$	
$C_4H_7^+$	$C_2H_3^+$	-28		$C_2H_3^+$	$C_2H_3^+$	$C_2H_3^+ + C_2H_6 \rightarrow C_4H_7^+ + H_2$	-46
	$C_2H_2^+$	-14			$C_2H_2^+$	$C_2H_2^+ + C_2H_6 \rightarrow C_4H_7^+ + H$	-42
$C_4H_9^+$	$C_2H_5^+$	-75	$C_3H_7^+$	$C_2H_5^+$		$C_2H_5^+ + C_2H_6 \rightarrow C_4H_9^+ + H_2$	-7
	$C_2H_3^+$	-3				$C_2H_3^+ + C_2H_6 \rightarrow C_2H_5^+ + C_2H_4$	-17

[a] Values are given as percentages of single-resonance intensities of observed species. [b] Reference 15. [c] Reference 12. [d] Reference 17.

state species, the reactant ions must be excited in our experiments, and/or the enhanced translational energies of the ions caused by the irradiating field may favor reaction. Note that virtually all the reactions are those of primary ions with ethane molecules. With the exceptions of $C_3H_3^+$ and $C_3H_5^+$, all the higher order ionic species appear to be unreactive toward this alkane.

Of special interest are the double-resonance spectra indicating the existence of protonated ethane and propane, $C_2H_7^+$ and $C_3H_9^+$. The yields of both ions were three to four times the abundances contributed by naturally occurring ^{13}C in $C_2H_6^+$ and $C_3H_8^+$, respectively. $C_2H_7^+$ was observed to be formed from $C_2H_6^+$, $C_2H_5^+$, and $C_2H_4^+$, while $C_3H_9^+$ was produced exclusively by reaction of $C_2H_6^+$. Because of the uncertainty of previous work[11,15] as to whether ground electronic or excited states of the $C_2H_6^+$ ions reacted with ethane molecules to yield the $C_2H_7^+$ species, the double-resonance signal of this ion was measured on irradiation of $C_2H_4^+$, $C_2H_5^+$, and $C_2H_6^+$ as the energy of the ionizing electrons was decreased in steps from 90 to 10 eV. The results of this experiment, which was conducted at an ethane pressure of 3.3×10^{-5} Torr, appear in Figure 2. The appearance potential of $C_2H_7^+$ formed from $C_2H_6^+$ is seen to be 12.0 eV. This value is near the literature value of the appearance potential of the $C_2H_6^+$ ion from ethane, 11.65 eV.[19] The agreement suggests that the reactant parent ion is either in its ground state or is slightly excited when it combines with C_2H_6 to give $C_2H_7^+$. On the other hand, the observed appearance potentials of $C_2H_7^+$ from $C_2H_4^+$ and $C_2H_5^+$, 16.5 and 20.5 eV, respectively, are much higher than the literature values for the appearance potentials of these primary ions in C_2H_6, 12.15 and 12.80 eV, respectively.[19] Though these large differences suggest that unlikely highly excited, long-lived $C_2H_4^+$ and $C_2H_5^+$ primary ions react with ethane to produce the protonated ethane, a more likely explanation probably lies in the possibility that the primary $C_2H_4^+$ and $C_2H_5^+$ formed directly by electron impact of ethane may not be involved in the creation of $C_2H_7^+$, but rather reactive excited product species of the same chemical composition are responsible. Since $C_2H_4^+$ is produced partially by collision dissociation of $C_2H_6^+$ and $C_2H_5^+$ almost exclusively by reaction of $C_2H_3^+$ with ethane, the overall reactions by which $C_2H_7^+$ is formed from these ions would be third order in ethane concentration. Ionization efficiency curves for the $C_2H_7^+$ ions would reflect the intensities of the primary $C_2H_6^+$ and $C_2H_3^+$ ions, which increase rapidly with the electron energy, and the distributions of states of excitation of the $C_2H_4^+$ and $C_2H_5^+$ products of the ion-molecule reactions. Both effects would contribute to the abnormally high appearance potentials for the $C_2H_7^+$ ion observed by the linear extrapolation method. Some evidence that this interpretation is plausible came from repetition of the experiment at a lower pressure (9.9×10^{-6} Torr) of C_2H_6 in the Syrotron cell. Then the double-resonance

(19) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 255.

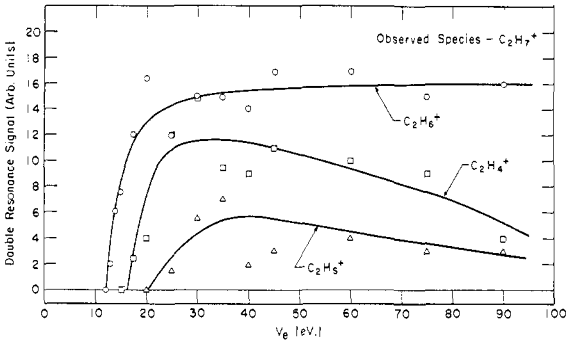

Figure 2. Variations of the double-resonance signals of $C_2H_7^+$ in gaseous ethane when $C_2H_6^+$, $C_2H_5^+$, and $C_2H_4^+$ were irradiated as the energy of the ionizing electrons was increased from 10 to 90 eV.

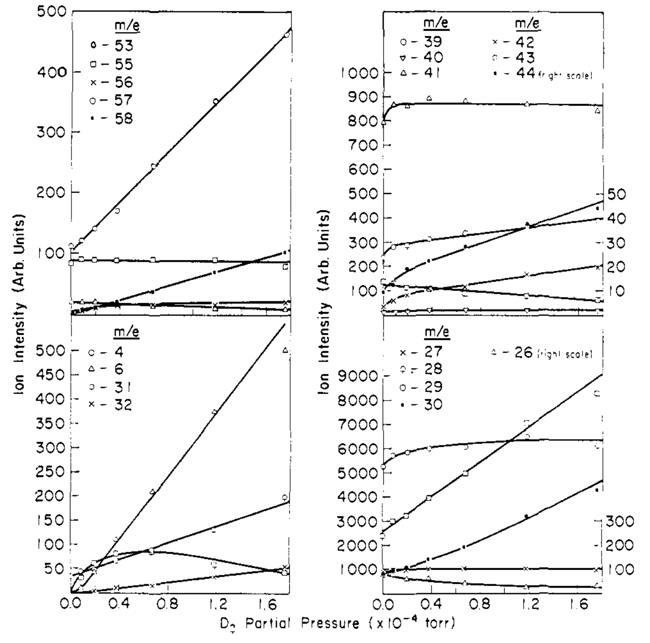

Figure 3. Intensities of several ions in C_2H_6–D_2 mixtures when the pressure of ethane was constant at 2.0×10^{-5} Torr and the pressure of deuterium was increased in steps from 0 to 1.8×10^{-4} Torr.

signals from the $C_2H_4^+$–$C_2H_7^+$ and $C_2H_5^+$–$C_2H_7^+$ pairs were too small to be observed, but irradiation of $C_2H_6^+$ gave a curve similar to the corresponding one in Figure 2. Quite possibly, at 9.9×10^{-6} Torr pressure of C_2H_6 the yields of $C_2H_4^+$ and $C_2H_5^+$ from ion–molecule reactions were too small, although their yields from ionization of ethane were moderate (see Figure 1), while at 3.3×10^{-5} Torr their concentrations as product ions were sufficient to observe double resonance signals.

Ethane–Hydrogen Mixtures. Indications of the extents to which deuterium atoms become incorporated in various organic ions as a result of reactions in gaseous C_2H_6–D_2 mixtures may be obtained from single-resonance studies in which the ethane pressure is held constant and the deuterium pressure is increased. The data from such an experiment appear in Figure 3, which shows the absolute intensities (in arbitrary units) of the major ions produced in mixtures of C_2H_6 at a pressure of 2.0×10^{-5} Torr and D_2 at pressures in the range from 0 to 1.8×10^{-4} Torr. Inspection of the plots reveals that the organic ions fall into two groups, one whose abundances remain virtually unchanged or may decrease with increasing D_2 concentration, and the other whose yields rise rapidly with added deuterium. Table II contains listings of the two series arranged according to mass-to-charge ratio (*m*/*e*) and corresponding probable chemical composition. It is obvious that a large number of deuterated ions are formed as products of ion–molecule reactions involving C_2H_6 and D_2.

To determine unambiguously how the deuterated organic species are formed, we observed the double-resonance spectra of the ions given in Table II. The results of the study in which the pressures of ethane and D_2 were 1.6×10^{-5} and 6.4×10^{-5} Torr, respectively, are tabulated in Table III. The magnitude of the double-resonance signal intensity relative to that of single resonance (column 5) is a measure of the extent of the reaction. In column 6 are presented the probable reactant gas molecules and in column 7 the probable neutral products of the important reactions giving rise to the data in Figure 3 and Table II. It will be noted that the reactions leading to the D-containing products are of the simple condensation and isotopic-exchange types, and are initiated both by D_2^+ and D_3^+, some of which have already been observed by Aquilanti and Volpi,[11] and by the hydrocarbon ions. Unfortunately, the double-resonance technique does not give unequivocal evidence for the direct reaction of D_2^+ with ethane in the presence of the mechanism which involves preliminary formation of D_3^+. Furthermore, the behaviors of the intensities of the two ions with increasing D_2 pressure (Figure 3) show only that D_3^+ is reactive toward ethane. The yield of D_2^+ increases to a maximum and then decreases, a characteristic indicating reaction with D_2, while that of D_3^+ rises linearly with deuterium concentration. If D_3^+ were unreactive, its yield would be expected to increase quadratically with the pressure of D_2. However, both modes of reaction with ethane have been included in column 6. The deuterated organic ions containing two carbon atoms react further with ethane to give labeled C_3 and C_4 product ions. If Table III is now studied in conjunction with Figure 3, one finds that the principal isotopic reactions in C_2H_6–D_2 mixtures in the range of concentrations investigated are those of D_2^+ with deuterium to form D_3^+, the reactions of these ions with

Table II. Behavior of Ionic Species in C_2H_6–D_2 Mixtures with Increasing D_2 Concentration

Organic species little affected by added D_2		Organic species whose abundances increase greatly with added D_2	
m/*e*	Probable species	*m*/*e*	Probable species[a]
26	$C_2H_2^+$	29	$C_2H_3D^+$
27	$C_2H_3^+$	30	$C_2H_4D^+$
28	$C_2H_4^+$, $C_2H_2D^+$	31	$C_2H_5D^+$
39	$C_3H_3^+$	32	$C_2H_6D^+$
40	$C_3H_4^+$	42	$C_3H_4D^+$
41	$C_3H_5^+$	44	$C_3H_6D^+$
43	$C_3H_7^+$	56	$C_4H_6D^+$
53	$C_4H_5^+$	57	$C_4H_7D^+$
55	$C_4H_7^+$	58	$C_4H_8D^+$

[a] Undeuterated ions with the same mass-to-charge ratios are also present.

ethane to give $C_2H_3D^+$, $C_2H_4D^+$, and $C_2H_5D^+$, and subsequent reactions of the latter to yield $C_4H_7D^+$ and $C_4H_8D^+$. In addition, the formation of $C_2H_2D^+$ from $C_2H_2^+$ and D_2 and of $C_3H_4D^+$ from $C_2HD^+ + C_2H_6$ appear to be prominent ionic reactions that are affected by the presence of D_2.

Similar studies were made on the isotopically inverse system C_2D_6–H_2. These served to confirm the results of the double-resonance experiments with C_2H_6–D_2 blends or to resolve ambiguities that arose in the identification of ionic species in these mixtures which possessed different chemical compositions but the same mass (*e.g.*, ions of mass 29, 30, 31, and 32). The observations are collected in Table IV. For this experiment the partial pressures of C_2D_6 and H_2 were 2.0×10^{-5} and 8.0×10^{-5} Torr, respectively. Comparison of Tables III and IV reveals that the double-resonance data are consistent in showing that the same chemical reactions are taking place in both isotopic gaseous mixtures. Note that simple isotopic exchange occurs in the reactions of several deuterated organic ions with H_2, particularly $C_2D_2^+$, $C_2D_3^+$, $C_2D_4^+$, $C_2D_5^+$, and $C_2D_6^+$.

The resolution of ambiguities concerning the chemical identities of some of the ionic species observed in C_2H_6–D_2 mixtures by studies on the isotopic inverse system may be illustrated by several examples. The species of mass 29 in the former blends may be $C_2H_5^+$ and/or $C_2H_3D^+$. The results on the C_2D_6–H_2 system (Table IV) shows that both species are present. But the product ion of mass 30 in the ethane–deuterium mixtures must be predominately $C_2H_6^+$, since the species of mass 33, and probably $C_2D_4H^+$, in the C_2D_6–H_2 blends has too low an abundance for observation of its double-resonance spectrum, and, accordingly, the equivalent ion $C_2H_4D^+$ (mass 30) in the normal mixture must also be in very small yield. Lastly, mass 31 in the latter consists of both $C_2H_7^+$ and $C_2H_5D^+$, because the corresponding ions can be distinguished and are present in the isotopic inverse mixture.

Unfortunately, the comparison of double-resonance spectra could not show definitely that doubly or triply labeled ethyl ions were present in the ethane–deuterium mixtures. Ionic species with masses corresponding to those moieties were observed in the inverse blends, but they could be ascribed to the formation of ethylenic ions. However, it would appear that multilabeled ethyl ions would not be formed readily from D_2^+ or $D_3^+ + C_2H_6$, because $C_2H_6D_2^+$ or $C_2H_6D_3^+$ complexes would be required as intermediates, species that are unlikely from valence-bond considerations. Furthermore, although isotopic exchange between primary (and possibly excited) $C_2H_5^+$ and D_2 occurred readily (see Tables III and IV), the subsequent exchange between $C_2H_4D^+$ and D_2 to give $C_2H_3D_2^+$ apparently did not take place. Though the data of Table III suggest that this reaction may occur, other reactions complicate the situation, and the equivalent reaction in C_2D_6–H_2 is not observed. (No double resonance was found between mass 32 (possibly $C_2D_3H_2^+$) observed and $C_2D_4H^+$ (mass 33) irradiated (see Table IV).) Similarly, mass 31 (possibly $C_2H_3D_2^+$) did not exchange with D_2 to give mass 32 (possibly $C_2H_2D_3^+$), as shown by the absence of a double-resonance signal connecting these species (Table III).

In an effort to understand the scavenging action of nitric oxide in the tritium–ethane system observed by Gant and Yang,[6] an experiment was performed in our Syrotron in which a blend of H_2 and C_2D_6 was held constant at 1.0×10^{-4} and 2.0×10^{-5} Torr, respectively, and NO was added in steps from 0 to 3.9×10^{-5} Torr. Comparison of the single-resonance spectra determined at each concentration of nitric oxide showed that the abundances of all species except those of masses 29, 30, and 62 decreased markedly as the partial pressure of NO increased. The yields of the three rose rapidly at first and then decreased. Apparently, the nitric oxide efficiently scavenges the charges on the ions in the system by exchange processes, but the subsequent reactions of NO^+ were not established because the species of masses 29 and 62 could not be identified in this experiment.

Discussion

Ionic Reactions in Ethane. Previous investigations of ion–molecule reactions in gaseous ethane by means of high-pressure mass spectrometry have led to conflicting conclusions on three aspects of its ion chemistry: the mechanisms of formation of $C_2H_4^+$ and $C_2H_5^+$ species, which are nominally primaries, the kinetic orders and modes of formation of products containing three and four carbons, and the existence of and mechanism of production of the protonated alkanes $C_2H_7^+$ and $C_3H_9^+$. Two methods were used to arrive at the reactant–product relationships involved in the formation of these species. Appearance potentials of the ions of interest were determined, and if they were reasonably close for a pair which were the respective reactant and product given by stoichiometry, a chemical reaction was assumed to have taken place. The second method was that of looking for a material balance among the ionic species as the pressure was varied. The former approach is subject to difficulties of interpretation when the appearance potentials of primary ions are not adequately separated in energy (which is the case in ethane) or excited states of the reactants are involved. Criticism of the reliability of the material balance method is justified when there are many reactants and products in a complex mass spectrum.

The results of the single-resonance, pressure-variation experiment (Figure 1) suggest that $C_2H_4^+$ at low Syrotron cell concentrations is indeed a reactive primary ion, but the constancy of its relative abundance above 1.0×10^{-5} Torr would point to its also being formed in an ion–molecule reaction. The double-resonance spectra for this ion (Table I) are evidence that it may be formed somewhat by reaction of the minor fragment $C_2H_2^+$. It is also produced by collisionally induced dissociation of the $C_2H_6^+$ parent (note the positive sign of the signal) when the latter is irradiated by an rf field, but it is doubtful that in the absence of such an irradiating field, a low-energy $C_2H_6^+$ would be decomposed by collision. The former observation is in agreement with that of Munson, *et al.*,[15] but we find no basis for concluding with Volpi, *et al.*,[12] that CH_2^+ is also a precursor. However, the production of $C_2H_4^+$ from $C_2H_2^+$ alone cannot account entirely for the constancy of its yield at higher pressures. Possibly, a fair fraction of the $C_2H_4^+$ formed directly by electron impact is unreactive with ethane.

Table III. Double-Resonance Spectra of Ions in D_2–C_2H_6 Mixtures

Species observed m/e	Species observed Ion	Species irradiated m/e	Species irradiated Ion	Double-resonance signal intensity[a]	Probable reactant gas molecule	Probable neutral products of reaction
6	D_3^+	4	D_2^+		D_2	D
26	$C_2H_2^+$	28	$C_2H_4^+$	−17	C_2H_6	H_2, C_2H_6
		29	$C_2H_5^+$ $C_2H_3D^+$	−12	C_2H_6	H_2, H, C_2H_6
		30	$C_2H_6^+$ $C_2H_4D^+$	−7	C_2H_6	H_2, C_2H_6
27	$C_2H_3^+$ C_2HD^+	26	$C_2H_2^+$	−3	C_2H_6	C_2H_5
		28	$C_2H_4^+$	−13	C_2H_6	C_2H_5, H_2
		29	$C_2H_5^+$	−5	C_2H_6	C_2H_6, H_2
		30	$C_2H_6^+$	−3	C_2H_6	C_2H_6, H_2, H
28	$C_2H_4^+$ $C_2H_2D^+$	26	$C_2H_2^+$	−2	C_2H_6 D_2	C_2H_4 D
		30	$C_2H_6^+$	+3	C_2H_6	C_2H_6, H_2
29	$C_2H_5^+$ $C_2H_3D^+$	4	D_2^+	−5	C_2H_6	H_2, HD
		6	D_3^+	−8	C_2H_6	D_2, H_2, H
		26	$C_2H_2^+$	−2	C_2H_6	C_2H_3
		27	$C_2H_3^+$	−9	C_2H_6	C_2H_4
		28	$C_2H_4^+$	−7	D_2	HD
		30	$C_2H_6^+$ $C_2H_4D^+$	−6	C_2H_6	C_2H_5D
30	$C_2H_6^+$ $C_2H_4D^+$	4	D_2^+	−6	C_2H_6	D_2
		6	D_3^+	−14	C_2H_6 C_2H_6	D_2, D H_2, D_2
		27	$C_2H_3^+$	−3	C_2H_6	C_2H_4
		28	$C_2H_4^+$	−20	D_2	D
		29	$C_2H_5^+$	−8	D_2	HD
31	$C_2H_7^+$ $C_2H_5D^+$	4	D_2^+	−18	C_2H_6	HD
		6	D_3^+	−28	C_2H_6	D_2, H
		29	$C_2H_5^+$	+5	D_2	D
		30	$C_2H_6^+$	−10	D_2 C_2H_6	HD C_2H_5
32	$C_2H_6D^+$	4	D_2^+	−18	C_2H_6	D
		6	D_3^+	−21	C_2H_6	D_2
		28	$C_2H_4^+$ $C_2H_2D^+$	−20	C_2H_6	C_2H_2
		29	$C_2H_5^+$	−12	D_2^c $C_2H_6^c$	D^c $C_2H_5^c$
			$C_2H_3D^+$		C_2H_6	C_2H_3
		30	$C_2H_6^+$	−14	D_2	D
39	$C_3H_3^+$	25	C_2H^+	−7	C_2H_6	CH_4
		26	$C_2H_2^+$	−16	C_2H_6	CH_3, H_2
		28	$C_2H_4^+$	+11	C_2H_6	CH_3, H_2
		29	$C_2H_5^+$	+7	C_2H_6	CH_4, H_2
40	$C_3H_4^+$	26	$C_2H_2^+$	−13	C_2H_6	CH_4
41	$C_3H_5^+$	26	$C_2H_2^+$	−19	C_2H_6	CH_3
		27	$C_2H_3^+$ C_2HD^+	−36	C_2H_6 C_2H_6	CH_4 CH_2D
		28	$C_2H_4^+$ $C_2H_2D^+$	+7	C_2H_6 C_2H_6	CH_3, H_2 CH_3D
		29	$C_2H_5^+$	+9	C_2H_6	CH_4, H_2
		39	$C_3H_3^+$	<-2	C_2H_6	C_2H_4
42	$C_3H_6^+$ $C_3H_4D^+$	26	$C_2H_2^+$	−14	D_2^c	HD^c
		27	C_2HD^+	−14	$C_2H_6^c$	CH_3^c
		28	$C_2H_2D^+$	−14	D_2^c $C_2H_6^c$	HD^c CH_4^c
43	$C_3H_7^+$	27	$C_2H_3^+$	−9	C_2H_6	CH_2
		28	$C_2H_4^+$	−37	C_2H_6	CH_3
		29	$C_2H_5^+$	−9	C_2H_6	CH_4
		41	$C_3H_5^+$	−5	C_2H_6	C_2H_4

Table III (*Continued*)

Species observed *m/e*	Species observed Ion	Species irradiated *m/e*	Species irradiated Ion	Double-resonance signal intensity[a]	Probable reactant gas molecule	Probable neutral products of reaction
44	$C_3H_6D^+$	30	$C_2H_4D^+$	−15	C_2H_6	CH_4
55	$C_4H_7^+$	26	$C_2H_2^+$	−18	C_2H_6	H
		27	$C_2H_3^+$	−21	C_2H_6	H_2
56	$C_4H_8^+$ [b]					
57	$C_4H_9^+$	28	$C_2H_4^+$	+10	C_2H_6	H
	$C_4H_7D^+$		$C_2H_2D^+$		C_2H_6	H
		29	$C_2H_5^+$	−64	C_2H_6	H_2
			$C_2H_3D^+$		C_2H_6	H_2
		30	$C_2H_6^+$	−9	C_2H_6	H_2, H
			$C_2H_4D^+$		C_2H_6	HD
58	$C_4H_8D^+$	29	$C_2H_5^+$	−7	D_2	HD
		30	$C_2H_4D^+$	−43	C_2H_6	H_2

[a] Values are given as percentages of single-resonance intensities of observed ions. Sign is the direction of the double-resonance relative to the single-resonance signal. [b] Ion intensity is too low to observe double resonance. [c] Two consecutive reactions are indicated by the double-resonance data.

The $C_2H_5^+$ ion, nominally a primary fragment arising from electron impact on ethane, exhibits the characteristics of a secondary ion (Figure 1). Data taken from double-resonance studies (Table I) show that the $C_2H_3^+$ species is principally responsible for its formation, with much smaller contributions to its production by $C_2H_4^+$ and $C_2H_2^+$. Note that $C_2H_6^+$ is not a reactant, in disagreement with the conclusions of Munson[15] and Volpi[12] that chemical reaction with a C_2H_6 molecule by the excited- or ground-state parent, respectively, is primarily responsible for the $C_2H_5^+$ in gaseous ethane. There is also considerable confusion in the literature on the roles of $C_2H_3^+$ and CH_3^+. Field and Lampe[13] postulated that both ions were precursors of $C_2H_5^+$, but Volpi[12] doubted that $C_2H_3^+$ was involved because a material balance indicated that C_3 and C_4 products were formed from this primary ion. We find a strong double resonance for $C_2H_3^+$ but none involving CH_3^+. CH_3^+ is highly reactive with ethane, and a plausible reaction would be hydride transfer giving $C_2H_5^+$. Probably, the very low concentration of methyl ions in ethane precludes observation of a double-resonance signal when $C_2H_5^+$ is formed predominantly by other processes. Finally, $C_2H_4^+$ must be an excited ion when it reacts to give $C_2H_5^+$, because the reaction of an ethylene ion in its ground state with an ethane molecule requires ~15 kcal/mol of energy.

From pressure-variation plots of their intensities, Munson, Franklin, and Field[15] decided that $C_3H_5^+$ was a secondary ion, $C_3H_7^+$ a third-order species, and $C_4H_9^+$ a quarternary ion, even though stoichiometry required only two ethane molecules for the formation of any of them. They concluded from their results that the reaction sequence of the three ions was $C_2H_5^+ \rightarrow C_3H_7^+ \rightarrow C_4H_9^+$. Our double-resonance results, on the contrary, show that $C_3H_7^+$ is produced principally by reaction of $C_2H_4^+$ with C_2H_6, and that $C_4H_9^+$ is formed directly from $C_2H_5^+$. Consequently, the sequential ionic reactions leading to $C_4H_9^+$ must be $C_2H_3^+ \rightarrow C_2H_5^+ \rightarrow C_4H_9^+$, this chain being concurrent with the $C_2H_4^+ \rightarrow C_3H_7^+$ reaction. On the other hand, the present results are in excellent agreement (see Table I) with the conclusions of Volpi's group[12] and of Fuchs.[17]

The protonated ethane ion $C_2H_7^+$ has been observed in small yield at high pressures in a mass spectrometer source[12,14,15] but not at low pressures.[13,16] To account for this species Volpi and his associates[12] proposed the reaction

$$C_2H_6^+ + C_2H_6 \longrightarrow C_2H_7^+ + C_2H_5 \qquad (1)$$

but Munson, *et al.*,[15] pointed out that this reaction is endoergic by greater than 20 kcal/mol, and so it is unlikely to occur. The latter workers also claimed that $C_2H_5^+$ and $C_2H_4^+$ cannot be the reactants involved because of the behaviors of their abundances as the ethane pressure is raised. Rather they concluded that the excited parent $(C_2H_6^+)^*$ must be the actual precursor of $C_2H_7^+$, and from the energetics of the reaction estimated that the heat of formation of $C_2H_7^+$ is $\leqslant 229$ kcal/mol and the proton affinity of ethane ~120 kcal/mol. In agreement with this work, we find (Table I) that $C_2H_6^+$ (probably excited) is indeed the main reactant giving $C_2H_7^+$, but we also find that $C_2H_5^+$ and $C_2H_4^+$ also contribute to its formation. Our double-resonance results on protonated propane $C_3H_9^+$ (Table I) suggest that it also exists, and that it is the product of the reaction of $C_2H_6^+$ with an ethane molecule. These observations are at variance with those from one high-pressure experiment,[15] but are in agreement with another.[12]

Ion Chemistry in D_2–C_2H_6 Mixtures. From his high-pressure mass spectrometric observations on C_2H_6-D_2 mixtures, Volpi[11] proposed that only a few ion–molecule reactions occur between species of the two components

$$D_3^+ + C_2H_6 \longrightarrow [C_2H_6D^+] + D_2 \qquad (2)$$

$$[C_2H_6D^+] \begin{array}{l} \nearrow C_2H_5^+ + HD \qquad (3a) \\ \searrow C_2H_4D^+ + H_2 \qquad (3b) \end{array}$$

$$C_2H_4D^+ + C_2H_6 \longrightarrow C_2H_5^+ + C_2H_5D \qquad (4)$$

The double-resonance spectra (Table III) confirm reactions 2, 3, and 4, but in addition to these other deuterated ionic products are formed by reaction of D_3^+ with C_2H_6, namely $C_2H_2D^+$ and $C_2H_3D^+$. Moreover, some of these species react further to give the deuterated

Table IV. Double-Resonance Spectra of Product Ions in H_2–C_2D_6 Mixtures

Species observed		Species irradiated[a]		Double-resonance signal intensity[b]	Probable reactant gas molecule	Probable neutral products of reactions
m/e	Ion	*m/e*	Ion			
3	H_3^+	2	H_2^+	−54	H_2	H
27	C_2DH^+	28	$C_2D_2^+$	−38	H_2	HD
28	$C_2D_2^+$	30	$C_2D_3^+$	−3	C_2D_6	C_2D_6, D
		32	$C_2D_4^+$	−16	C_2D_6	C_2D_6, D_2
		34	$C_2D_5^+$	−7	C_2D_6	C_2D_6, D_2, D
		36	$C_2D_6^+$	−2	C_2D_6	C_2D_6, D_2
29	$C_2D_2H^+$	33	$C_2D_4H^+$	+7	C_2D_6	C_2D_6, D_2
30	$C_2D_3^+$	28	$C_2D_2^+$	−2	C_2D_6	C_2D_5
		32	$C_2D_4^+$	−15	C_2D_6	C_2D_6, D
		34	$C_2D_5^+$	−5	C_2D_6	C_2D_6, D_2
		36	$C_2D_6^+$	−2	C_2D_6	C_2D_6, D_2, D
31	$C_2D_3H^+$	32	$C_2D_4^+$	−8	H_2	HD
32	$C_2D_4^+$	28	$C_2D_2^+$	−1	C_2D_6	C_2D_4
		36	$C_2D_6^+$	+5	C_2D_6	C_2D_6, D_2
33	$C_2D_4H^+$	30	$C_2D_3^+$	−2	C_2D_6[d] H_2[d]	C_2D_4[d] HD[d]
		32	$C_2D_4^+$	−18	H_2	H
		34	$C_2D_5^+$	−9	H_2	HD
34	$C_2D_5^+$	28	$C_2D_2^+$	+2	C_2D_6	C_2D_3
		30	$C_2D_3^+$	−6	C_2D_6	C_2D_4
		32	$C_2D_4^+$	+6	C_2D_6	C_2D_5
		33	$C_2D_4H^+$	−5	C_2D_6	C_2D_5H
35	$C_2D_5H^+$	34	$C_2D_5^+$	−10	H_2	H
		36	$C_2D_6^+$	−16	H_2	HD
36	$C_2D_6^+$	28	$C_2D_2^+$	+2	C_2D_6	C_2D_2
		32	$C_2D_4^+$	−1	C_2D_6	C_2D_4
		35	$C_2D_5H^+$	−3	C_2D_6	C_2D_5H
37	$C_2D_6H^+$	32	$C_2D_4^+$	−14	C_2D_6[d] H_2[d]	C_2D_4[d] H[d]
		34	$C_2D_5^+$	−14	H_2[d] C_2D_6[d]	H[d] C_2D_5[d]
		36	$C_2D_6^+$	−40	H_2	H
38	$C_2D_7^+$	36	$C_2D_6^+$	−26	C_2D_6	C_2D_5
42	$C_3D_3^+$	26	C_2D^+	−6	C_2D_6	CD_4
		28	$C_2D_2^+$	−9	C_2D_6	CD_3, D_2
		30	$C_2D_3^+$	+6	C_2D_6	CD_4, D_2
		32	$C_2D_4^+$	+10	C_2D_6	CD_3, D_2
		34	$C_2D_5^+$	+7	C_2D_6	CD_4, D_2
43	$C_3D_3H^+$[c]					
44	$C_3D_4^+$	28	$C_2D_2^+$	−23	C_2D_6	CD_4
45	$C_3D_4H^+$	26	C_2D^+	−7	H_2[d] C_2D_6[d]	H[d] CD_3[d]
		27	C_2DH^+	−21	C_2D_6[d]	CD_3[d]
		28	$C_2D_2^+$	−22	H_2[d]	HD[d]
		29	$C_2D_2H^+$	−11	C_2D_6[d]	CD_4[d]
		30	$C_2D_3^+$	−6	H_2[d]	HD[d]
		32	$C_2D_4^+$	+4	H_2[d] C_2D_6[d]	HD[d] C_2H_5[d]
46	$C_3D_5^+$	27	C_2DH^+	−2	C_2D_6	CD_2H
		28	$C_2D_2^+$	−16	C_2D_6	CD_3
		29	$C_2D_2H^+$	−2	C_2D_6	CD_3H
		30	$C_2D_3^+$	−30	C_2D_6	CD_4
		32	$C_2D_4^+$	+19	C_2D_6	CD_4, D
		34	$C_2D_5^+$	+5	C_2D_6	CD_4, D_2
		42	$C_3D_3^+$	<−2	C_2D_6	C_2D_4
48	$C_3D_6^+$[c]					
49	$C_3D_6H^+$	33	$C_2D_4H^+$	−12	C_2D_6	CD_4
50	$C_3D_7^+$	30	$C_2D_3^+$	−8	C_2D_6	CD_2
		32	$C_2D_4^+$	−11	C_2D_6	CD_3
		34	$C_2D_5^+$	−8	C_2D_6	CD_4
		46	$C_3D_5^+$	−6	C_2D_6	C_2D_4
62	$C_4D_7^+$	28	$C_2D_2^+$	−16	C_2D_6	D
		30	$C_2D_3^+$	−20	C_2D_6	D_2
63	$C_4H_7D^+$[c]					
64	$C_4D_8^+$[c]					
65	$C_4D_8H^+$	33	$C_2D_4H^+$	−36	C_2D_6	D_2
		34	$C_2D_5^+$	−21	H_2[d] C_2D_6[d]	HD[d] D_2[d]
66	$C_4D_9^+$	32	$C_2D_4^+$	+3	C_2D_6	D
		34	$C_2D_5^+$	−73	C_2D_6	D_2
		36	$C_2D_6^+$	<−2	C_2D_6	D_2, D

[a] Except for the H_2^+–H_3^+ pair, these two species could not be irradiated when the other ions were observed. [b] Values are given as percentages of single-resonance intensities of observed ions. Sign is the direction of the double-resonance relative to the single-resonance signal. [c] Ion intensity too small to measure double resonance accurately. [d] Two consecutive reactions are indicated by the double-resonance data.

C_3 and C_4 ions $C_3H_4D^+$, $C_3H_6D^+$, $C_4H_6D^+$, $C_4H_7D^+$, and $C_4H_8D^+$.

The rather simple two- or three-step processes in gaseous ethane found in this study contrast greatly with the situation in methane. In the latter, the very high reactivity of the methyl ion with both D_2 and CH_4 is the reason for the complex sequence of consecutive and competitive ion–molecule reactions observed.

Mechanism of Wilzbach Labeling of Ethane. A limited investigation of self-induced tritiation of ethane in C_2H_6–T_2 gaseous mixtures by Gant and Yang[6] revealed that 77% of the C_2H_5T product formed was not scavenged by nitric oxide, whereas all the tritiated propane and *n*-butane also produced were quenched by this scavenger. Furthermore, irradiation of these mixtures by γ rays greatly accelerated production of labeled propane and butane, but did not affect the yield of tritiated ethane. Gant and Yang therefore concluded that the unaffected 77% of the yield of C_2H_5T was the result of ionic reactions beginning with the T^3He^+ or T^+ daughter formed directly by the nuclear transformation of T_2. Since molecular tritium gives T^3He^+ following more than 90% of the β transitions,[20] it, rather than T^+, is probably the primary precursor.

In the experiments of Cacace, Cipollini, and Ciranni[7] on the C_2H_6–T_2 system, their conditions were such that only the decay-induced mode of formation of tritiated compounds was possible. The major products were labeled methane and ethane, with yields of 14 and 34–36%, respectively. To account for their results, these investigators proposed that the tagged ethane is formed by the sequences of ionic reactions

$$T_2 \longrightarrow T^3He^+ + \beta^- + \nu \tag{5}$$

$$(T^3He)^+ + C_2H_6 \longrightarrow (C_2H_6T)_{exc}^+ + {}^3He \tag{6}$$

$$(C_2H_6T^+)_{exc} + M \longrightarrow C_2H_6T^+ + M \tag{7}$$

$$C_2H_6T^+ + C_2H_6 \longrightarrow C_2H_5T + C_2H_7^+ \tag{8}$$

and/or

$$(C_2H_6T)_{exc}^+ \longrightarrow C_2H_4T^+ + H_2 \tag{9}$$

$$C_2H_4T^+ + C_2H_6 \longrightarrow C_2H_5T + C_2H_5^+ \tag{10}$$

The CH_3T among their products was considered to be mainly produced in the series of reactions

$$(C_2H_6T^+)_{exc} \longrightarrow C_2H_2T^+ + 2H_2 \tag{11}$$

$$C_2H_2T^+ + C_2H_6 \longrightarrow CH_3T + C_3H_5^+ \tag{12}$$

The single- and double-resonance behavior of the ions in C_2H_6–D_2 gaseous mixtures (Table III; see also Table IV), however, would suggest that $C_2H_6T^+$ does not undergo proton transfer with ethane *via* reaction 8, since no double resonance of $C_2H_7^+$ was observed with $C_2H_6D^+$. Rather, our data indicate that the deuterated ethane ion does not react with ethane, and consequently, we suggest that tritiated ethane may be formed by neutralization of the corresponding $C_2H_6T^+$ species

$$C_2H_6T^+ + e^-(M) \longrightarrow C_2H_5T + H + M^+ \tag{13}$$

However, the yields of the $C_2H_7^+$ and $C_2H_6D^+$ observed in our experiments are rather low compared with $C_2H_6^+$ and $C_2H_4D^+$ (see Figure 3), and this finding plus our double-resonance data indicate that the mechanism suggested by Cacace involving hydride transfer to $C_2H_4T^+$ (reaction 10) is a more likely way of forming tritiated ethane. In addition, we find strong evidence (see the spectra for $C_2H_3^+$ and $C_2H_2D^+$ in Table III) to support Cacace's proposed mechanism of formation of CH_3T (reaction 12). It appears that excited $C_2H_6T^+$ formed by reaction of the T^3He^+ daughter from the β decay of T_2 mainly dissociates into $C_2H_4T^+$ or $C_2H_2T^+$, and these ions then react further with ethane molecules to yield tritiated ethane and methane, respectively.

In ethane containing a small fraction of T_2, tritiated propane and butane should be almost entirely the end result of radiation-induced ionic and free-radical reactions

$$C_2H_3^+ + C_2H_6 \longrightarrow C_2H_5^+ + C_2H_4 \tag{14}$$

$$C_2H_5^+ + C_2H_6 \longrightarrow C_4H_9^+ + H_2 \tag{15}$$

$$C_2H_4^+ + C_2H_6 \longrightarrow C_3H_7^+ + CH_3 \tag{16}$$

$$C_3H_7^+ + M \longrightarrow C_3H_7 + M^+ \tag{17}$$

$$C_4H_9^+ + M \longrightarrow C_4H_9 + M^+ \tag{18}$$

$$C_3H_7 + T_2 \longrightarrow C_3H_7T + T \tag{19}$$

$$C_4H_9 + T_2 \longrightarrow C_4H_9T + T \tag{20}$$

Very small yields of C_3H_7T and C_4H_9T should also be produced by successive reactions of T_2^+ with ethane to give $C_2H_3T^+$ and $C_2H_4T^+$, combination of the latter ions with C_2H_6 to form $C_3H_6T^+$ and $C_4H_8T^+$, neutralization of the ions to labeled propyl and butyl radicals, respectively, and hydrogen abstraction by the radicals. Reactions 19 and 20 and the equally slow hydrogen-abstraction reactions of the tritiated propyl and butyl radicals could easily be quenched by nitric oxide scavenging. The mechanisms proposed therefore can explain Gant and Yang's[6] results on the influence of NO on the production of tritiated propane and butane.

Our observations on the effect of NO on the ionic species in C_2D_6–H_2 mixtures would suggest that all the ionic reactions may be hindered by charge exchange to this scavenger. However, if the nitric oxide is present in small percentage, it may not be able to interfere with the ionic reactions 6–12, but it could act as the neutralizing agent for $C_2H_6T^+$ in reaction 13. Consequently, NO should not significantly reduce the yield of C_2H_5T, a conclusion in accordance with the observations of Gant and Yang.

It is of interest to note that the most prominent C_4 ion at high D_2 concentrations is the unsaturated species $C_4H_7D^+$ (mass 57, Figure 3). Neutralization of the equivalent ion in a C_2H_6–T_2 mixture should yield tritiated butenes. That labeled butenes were not observed by Gant and Yang may be due to the low concentration of T_2 in their systems. $C_4H_7D^+$ is formed from $C_2H_3D^+$ which was produced by reactions of D_2^+ and D_3^+ with ethane and by reaction of $C_2H_4^+$ with D_2 (Table III). At low concentration of T_2 in gaseous ethane, the yield of $C_2H_3T^+$ from the former processes would be very low, and since $C_2H_4^+$ would be depleted by reaction with ethane molecules, there would be little $C_2H_3T^+$ formed by the latter mode also.

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[20] S. Wexler, *J. Inorg. Nucl. Chem.*, **10**, 8 (1959); see also A. H. Snell, F. Pleasonton, and H. E. Leming, *ibid.*, **5**, 112 (1957).