of 1.2 Å to about 1.6 Å or greater during the collision.

The low yield of $O(^1D)$ in the reaction of Xe* with O_2 should be compared to photodissociation at 149 nm, where $O(^3P) + O(^1D)$ is the major product.[15] According to the calculated potential energy curves, formation of these products in the reaction with Xe* requires a vertical excitation of O_2 to $O_2(B^3\Sigma_u^-)$ (as in photolysis) or excitation to a group of $^3\Sigma_u^-$ and $^3\Pi_u$ states, which are all repulsive and would again require stretching of the O–O bond to 1.6 Å, if the entire excitation energy, 8.3 eV, of Xe* is transferred to O_2 (still greater stretching is required if less energy is transferred). Clearly, the results indicate that this stretching is achieved efficiently in neither the Ar* + O_2 nor the Xe* + O_2 collisions. A single $^3\Sigma_g^-$ state, which correlates with $O(^3P) + O(^1D)$, extends to smaller internuclear distances but is likely to be predissociated by a $^3\Pi_g$ state, which crosses it and correlates with $O(^3P) + O(^3P)$. In contrast, a smaller stretching of the O–O bond allows access to $^1\Pi_{u,g}$ and $^3\Pi_{u,g}$ states, which correlate with $O(^3P) + O(^3P)$. We conclude, therefore, that this is the major route for the Xe* + O_2 reaction.

A possible mechanism for such bond stretching during the approach of Xe* and O_2 is provided by an initial electron jump to yield a charge-transfer intermediate, $Xe^+O_2^-$, which is favored by the positive electron affinity of O_2.[29] Such a charge-transfer mechanism has been invoked previously[30] to explain the rapid quenching of excited alkali (^2P) atoms by O_2. As the equilibrium bond length of O_2^- is about 1.35 Å,[18] vibration of the newly formed O_2^- over the bond length range 1.2–1.5 Å may result. Access to the charge-transfer intermediate should be open to all reagent surfaces except possibly those with quintet spin multiplicity ($Xe^+(^2P) + O_2^-(^2\Pi)$ yields singlet and triplet surfaces only). However, if such surfaces lead to excitation of quintet states of O_2, these will again dissociate to $O(^3P) + O(^3P)$.

Ungerade states of O_2 correlating with $O(^3P) + O(^1D)$ should be accessible to collisions of O_2 with Kr*, which has an excitation energy of 10 eV, and thus, from the arguments given above, a small but significant yield of $O(^1D)$ would be expected from this reaction.

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Protonation of C_3H_6 Isomers: Isotope Exchange and Isomerization

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Isotope exchange processes of the type ($MH^+ + C_3D_6 \rightarrow MD^+ + C_3HD_5$) or ($MD^+ + C_3H_6 \rightarrow MH^+ + C_3H_5D$) (where $C_3(H,D)_6$ is propylene or cyclopropane) have been studied in an ICR spectrometer. It is shown that, for both reactant molecules, the efficiency of the exchange reaction can be correlated with the exothermicity of the formation of the complex $[M{\cdot}C_3(H,D)_7^+]$ from separated $M(H,D)^+$ and $C_3(H,D)_6$ reactants. In the case of propylene, all of the $M(H,D)^+$ reactants are chosen so that proton (deuteron) transfer is endothermic. For cyclopropane reactant molecules, some of the reactant pairs have available an exothermic channel leading to the formation of a *sec*-propyl ion product, but this process is shown to compete poorly with the isotope exchange process (which may or may not involve isomerization of the neutral cyclopropane to propylene in the collision complex). Isotope exchange reactions involving the partially deuterated propylenes $CD_3CH{=}CH_2$, $CH_3CH{=}CD_2$, and $CH_3CH{=}CHD$ provide evidence that, when M is a nitrile, there is statistical scrambling of the H and D atoms in the $C_3(H,D)_7^+$ in the $[M{\cdot}sec\text{-}C_3(H,D)_7^+]$ complex; when M is an aldehyde or a formate, the reaction involves only the H and D atoms on the methyl groups of the *sec*-$C_3(H,D)_7^+$ species in that complex. Experiments with 1,1-$C_3D_2H_4$ indicate that the isotope exchange process involves a single $C(H,D)_2$ group in the cyclopropane molecule, except when proton transfer is exothermic. Rate constants are reported for a number of proton-transfer reactions involving cyclopropane.

Introduction

Recent work in a number of laboratories[1-4] has explored the mechanisms and kinetics of thermoneutral isotope exchange processes such as

$$MD^+ + AH \rightarrow MH^+ + AD \qquad (1)$$

or analogous processes involving anions.[3,5-9] The mechanism of reaction 1 is generally accepted[1-9] to involve the transfer of a deuteron (proton) within the complex, fol-

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TABLE I: Rate Constants of the Reactions $MH^+ + CD_3CD{=}CD_2 \rightarrow MD^+ + C_3D_5H$ and $MD^+ + CH_3CH{=}CH_2 \rightarrow MH^+ + C_3H_5D$, and Energetics of Related Processes

reactants	$10^{-8}r$,[a] cm	μ_D, M[b]	$10^{10}k$, cm^3/(molecule s)	k/Z[e]	ΔH, kcal/mol	
					H^+ or D^+ transfer[f]	[M·*sec*-$C_3(H,D)_7^+$] formation[g]
$CD_3CND^+ + CH_3CH{=}CH_2$	3.7	3.9	8.3[c]	0.67	+6.6	−18
$C_2H_5CNH^+ + CD_3CD{=}CD_2$	3.6	4.0	8.1[c]	0.75	+10.1	−17
n-$C_3H_7CNH^+ + CD_3CD{=}CD_2$	3.9	4.1	5.3[c]	0.49	+11.4	−13
i-$C_3H_7CNH^+ + CD_3CD{=}CD_2$	3.9	4.1	4.1[c]	0.38	+12.3	−12
$CD_3CDOD^+ + CH_3CH{=}CH_2$	3.5	2.7	7.3[c] 5.0[d]	0.54 0.41	+4.7	−16
$(HCOOCH_3)H^+ + CD_3CD{=}CD_2$	3.5	1.8	3.4[c]	0.31	+7.8	−9
$(HCOOC_2H_5)H^+ + CD_3CD{=}CD_2$	3.6	1.9	1.2[c]	0.11	+11.5	−6
$(HCOOCH_2CH_2CH_3)H^+ + CD_3CD{=}CD_2$	3.7	1.9	0.7[c]	0.067	+12.8	−4

[a] Assumed collision diameter. Used for calculation of well depth associated with [M·*sec*-$C_3(H,D)_7^+$] complex with eq 12. See footnotes 12 and 13. [b] Dipole moment of M from A. A. Maryott and F. Buckley, *Natl. Bur. Stand. Cir.* No. 537 (1953). [c] 330 K. [d] 403 K. [e] Collision rate constants estimated by using formulations given in ref 11. [f] Relative proton affinity scale from ref 19 and references cited therein. [g] Exothermicity of the process $MH^+ + C_3(H,D)_6 \rightarrow$ [M·*sec*-$C_3(H,D)_7^+$] estimated from well depth of complex relative to separated *sec*-$C_3H_7^+$ + M reactants and endothermicity of proton transfer from MH^+ to propylene.

lowed by a transfer back to the original proton donor, and the dissociation of the complex to give isotopically scrambled products which are chemically identical with the original reactants:

$$MD^+ + AH \underset{b}{\overset{Z}{\rightleftarrows}} [MD^+{\cdot}AH] \xrightarrow{c} [M{\cdot}AHD^+] \xrightarrow{d} [MH^+{\cdot}AD] \xrightarrow{e} MH^+ + AD \quad (2)$$

In most cases studied, the deuteron transfer reactions from MD^+ to AH (or the analogous proton-transfer reactions) were endothermic,[1-4] although such isotope exchange processes have been shown to occur in competition with proton-transfer reactions, when those reactions do not occur at the collision rate.[4] In the study from this laboratory,[4] it was shown that when the formation of the $[M{\cdot}AHD^+]$ complex from separated reactants is predicted to be thermoneutral or endothermic, reaction 1 occurs with a low probability or not at all. It was further shown that when AH is a molecule which would be expected to direct electrophilic attack to a position in the molecule favorable for proton transfer, the efficiency of reaction is increased relative to molecules for which this is not the case.

The present study represents an extension of the earlier work in order to clarify some of the features of the interpretation. Here we will examine reactions 3 and 4. In

$$MD^+ + CH_3CH{=}CH_2 \rightarrow MH^+ + C_3H_5D \quad (3)$$

$$MH^+ + CD_3CD{=}CD_2 \rightarrow MD^+ + C_3D_5H \quad (4)$$

this series of experiments, by keeping the identity of the neutral reactant (propylene) constant, factors influencing the orientation of the ion in the complex (i.e., factors influencing k_c in mechanism 2) will be the same for different proton (deuteron) donors, so that the effects of other parameters on the probability of a reactive collision can be pinpointed. Details of the mechanism will be explored by examining isotope exchange processes with partially deuterated propylenes.

Additional experiments involving cyclopropane are included. In addition to reaction 1, these systems have available other reaction channels, such as the exothermic rearrangement of the hydrocarbon molecule

$$MD^+ + c\text{-}C_3H_6 \rightarrow M(H,D)^+ + C_3(H,D)_6 \text{ (propylene)} \quad (5)$$

or, in some cases, the deuteron transfer

$$MD^+ + c\text{-}C_3H_6 \rightarrow sec\text{-}C_3H_6D^+ + M \quad (6)$$

Experimental Section

The rate constants were measured with a pulsed ICR spectrometer, the operation and construction of which have been described in detail elsewhere.[10] Briefly, ions are produced by bombarding a gaseous sample (pressure, 10^{-6}–10^{-5} torr) with a 20-eV electron pulse of about 4-ms duration, and then are trapped by an electrostatic potential well between the walls of the ICR cell. The relative concentrations of the ions of interest were recorded as a function of time. The gases introduced to the ICR spectrometer were either premixed and admitted through a single inlet or were admitted separately through two inlets. For measuring the rate constants of reactions 3 and 4, roughly 5:1 mixtures of M–$C_3(H,D)_6$ were used. Similar mixtures were used for the other hydrocarbons studied here. The bombarding electrons mainly produce the radical ions, M^+, which react with the M molecules to form the protonated or deuterated ions, MH^+ or MD^+ (depending on whether the molecule M is deuterated), which are the reactant ions in reactions 1–6. In the experiments examining the relative rate constants, k_H/k_D, for H/D exchange with partially deuterated propylenes, approximately equimolar M–$C_3(H,D)_6$ mixtures were used.

The bimolecular exchange rate constants were obtained from the slope of a plot of pseudo-first-order rate constants vs. the number density of the hydrocarbon. These plots gave good straight lines through the origin (within one standard deviation of a linear regression analysis) over at least a sixfold change in number density, indicating the absence of any pressure dependence of the bimolecular rate constants. All reactant ions were examined in the absence of added hydrocarbon as a function of time, and unreactive decay, if any, was routinely corrected for.

The analyzer cell of the ICR can be externally heated, and the temperature in the cell is routinely monitored by thermocouples attached to the cell in the vicinity of the filament and on the opposite side of the cell. The observed temperature gradient across the cell for the experiments described here was 20–25 °C. The effective temperature of the reacting species has been calibrated by comparing equilibrium constants determined in the instrument with corresponding equilibrium constants measured in a photoionization mass spectrometer. It was found that typically the temperature of the reactants appeared to correspond to a temperature about 5–10 °C above the temperature of

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the "cool" side of the cell. The entire gas-handling system, from the inlet system to the analyzer cell, is maintained at the same temperature to ensure that the gas in the chamber is at the measured temperature.

Results and Discussion

H/D Exchange Reactions Involving Propylene. Table I gives the rate constants measured for the isotope exchange processes 3 and 4 for a number of different reactant ions. The probability that a collision will lead to reaction (the reaction efficiency, k/Z, where Z is the rate constant for collision) is also given. The collision rate constants were calculated by using the formulations described in ref 11; because the dipole moment of propylene is very small, 0.35 D, the values of Z do not differ significantly for the different calculational approaches.

For all the reactant pairs listed in Table I, the H/D exchange reaction was the only reaction observed, except for a small amount of association of the protonated species with its polar precursor. This latter process accounted for less than 5% of the loss of the reactant ions; the reported rate constants have been routinely corrected for the occurrence of such processes. Table I also gives the enthalpy changes for the proton (deuteron) transfer processes involving the following sets of reactants:

$$MD^+ + CH_3CH{=}CH_2 + sec\text{-}C_3H_6D^+ + M \qquad (7)$$

$$MH^+ + CD_3CD{=}CD_2 \rightarrow sec\text{-}C_3D_6H^+ + M \qquad (8)$$

Reactions 7 or 8 are endothermic by at least 5 kcal/mol for the reactant pairs listed in Table I, and it is therefore not surprising that there was no evidence indicating the formation of propyl ions in these systems. (For example, double resonance ejection experiments in which propyl ions would have been ejected had no effect on the product ions of reactions 3 or 4.)

If we compare members of a homologous series of M compounds in Table I, it is a general observation that the more efficient reactions tend to be those for which the corresponding proton transfer is least endothermic. However, there does not appear to be any real correlation with the ΔH of the proton-transfer reaction, although such relationships have been observed before.[3] It does appear (Table I) that if one compares reactant pairs for which the endothermicity of proton transfer is similar, the efficiency of the exchange appears to be greater the larger the dipole moment of M. This suggests that the depth of the potential well of the $[M{\cdot}AHD^+]$ complex may be a factor which influences the efficiency of the isotope exchange process. In the earlier work from this laboratory,[4] it was suggested that the energetics of transferring a proton (deuteron) in the complex might influence the efficiency of the exchange process:

$$MD^+ + AH \rightarrow [MD^+{\cdot}AH] \rightarrow [M{\cdot}AHD^+] \qquad (9)$$

$$MH^+ + AD \rightarrow [MH^+{\cdot}AD] \rightarrow [M{\cdot}ADH^+] \qquad (10)$$

The exothermicity of processes 9 and 10 is just

$$\Delta H(9,10) = \Delta H(\mathrm{PT}) + W \qquad (11)$$

the endothermicity of the proton transfer reaction, ΔH(PT), plus W, the exothermicity of the formation of the $[M{\cdot}sec\text{-}C_3(H,D)_7^+]$ complex from separated ($sec\text{-}C_3(H,D)_7^+$ + M) reactants. These relationships are illustrated in the reaction coordinate diagram shown in Figure 1. Although a quantum mechanical calculation of the potential well depth for these complexes is outside the scope of this paper, it was shown in the previous paper from this laboratory[4] that a rough estimate of the quantity W can be obtained[12] by simply evaluating the classical potential of interaction between the ion and molecule at a distance corresponding to the collision diameter, r[13]

$$W(r) = -q\mu_D/r^2 - q^2\alpha/2r^4 \qquad (12)$$

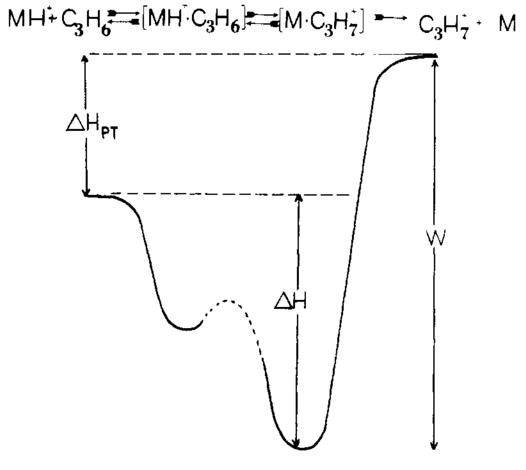

Figure 1. Reaction coordinate diagram for the reaction $MH^+ + CH_3CH{=}CH_2 \rightleftarrows [MH^+{\cdot}CH_3CH{=}CH_2] \rightleftarrows [M{\cdot}sec\text{-}C_3H_7^+] \rightleftarrows sec\text{-}C_3H_7^+ + M$. Relative energy levels as depicted are typical for reactants observed here (Table I). The enthalpy change for proton transfer is ΔH_{PT}, and the enthalpy change for formation of the $[M{\cdot}sec\text{-}C_3H_7^+]$ complex from separated reactants is also designated.

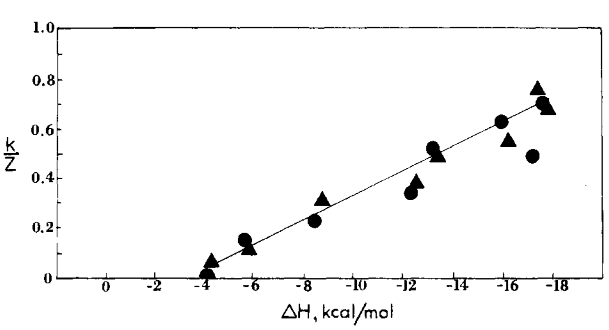

Figure 2. The probability of a reactive collision, k/Z, for $M(H,D)^+$ + propylene (▲) and $M(H,D)^+$ + cyclopropane (●) reactant pairs as a function of the exothermicity for the formation of the $[M{\cdot}C_3(H,D)_7^+]$ complex from separated reactants. Well depths for the complexes were estimated with eq 12 (see Discussion and footnotes 12 and 13).

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(12) For $[NH_4^+{\cdot}NH_3]$ eq 12 predicts a well depth of −23 kcal/mol, compared with an experimental value of −25 kcal/mol (P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977)); for $[H_3O^+{\cdot}H_2O]$ the calculated value is −33 kcal/mol, compared with −32 kcal/mol from experiment (*Ibid.*); for $[C_6H_6^+{\cdot}c\text{-}C_6H_{12}]$ the calculated value is −6 kcal/mol, compared with −10 kcal/mol from experiment (M. Meot-Ner, P. Hamlet, E. P. Hunter, and F. H. Field, *J. Am. Chem. Soc.*, **100**, 5466 (1978)); for $[C_6H_6^+{\cdot}CS_2]$ one calculates −11 kcal/mol, to be compared with an experimental value of −12 kcal/mol (from Meot-Ner et al.). Professor Joel Liebman has pointed out to the authors that eq 12 (with values of r chosen as described here) gives values in surprisingly good agreement with experiment for $\Delta H_f(C_2H_7^+)$ if that ion is seen as a $[C_2H_5^+{\cdot}H_2]$ complex (calculated, 216 kcal/mol; experimental, 214 kcal/mol, from K. Hiroaka and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 6119 (1976)); for $C_3H_9^+$ if that ion is seen as a $[C_2H_5^+{\cdot}CH_4]$ complex (calculated, 195 kcal/mol; experimental, >189 kcal/mol from Hiroaka and Kebarle); and for the reaction enthalpies of the reactions $t\text{-}C_4H_9^+ + H_2 \rightarrow C_4H_{11}^+$ (calculated, −1.8 kcal/mol and experimental, −1 kcal/mol) and $sec\text{-}C_4H_9^+ + H_2 \rightarrow C_4H_{11}^+$ (calculated, −4.4 kcal/mol and experimental, −3.4 kcal/mol, both from Hiroaka and Kebarle). The use of this formulation also leads to reasonably close estimates of some proton affinities, for instance, that of 2-propanol if the protonated ion is taken to be equivalent to a $[sec\text{-}C_3H_7^+{\cdot}H_2O]$ complex (calculated proton affinity, 182 kcal/mol and experimental, 188 kcal/mol).

TABLE II: Rate Constants at 335 K for the Reactions

$$MH^+ + c\text{-}C_3H_6 \underset{b}{\overset{a}{\rightleftarrows}} C_3H_7^+ + M$$

M	PA,[a] kcal/mol	$10^{10}k_a$, cm^3/(molecule s)	k_a/Z_a[b]	$10^{10}k_b$, cm^3/(molecule s)	ΔH_a (sec-$C_3H_7^+$ product), kcal/mol
H_2S	171.7	12.7	1.0		−15.6
HCOOH	178.1	4.7 ± 1.0	0.41	~1[c] 1.1[d]	−9.2
AsH_3	178.0	4.8 ± 0.4	0.48	~1[c] 0.97[d]	−9.3
CH_3OH	178.6	2.6 ± 0.2	0.20	reacts[c] 7.1 ± 0.4[d]	−8.7
CH_3CHO	184.2	1.7 ± 0.7	0.15	reacts[c] 16.0 ± 0.4[d]	−3.1
CH_3CN	186.1		no reaction		−1.2
C_2H_5CHO	187.0		no reaction		−0.3
$HCOOCH_3$	187.3		no reaction		0

[a] Relative proton affinity scale from ref 19 and references cited therein. Absolute values assigned as described in ref 18. [b] Collision rate constants calculated according to formulations described in ref 11. [c] This work. [d] Values from ref 19 for proton transfer from sec-$C_3H_7^+$ to M.

where q is the electronic charge, μ_D is the dipole moment, and α is the polarizability of the neutral reactant partner. Although the estimation of W from eq 12 neglects close-range attractive and repulsive interactions, as well as the anisotropy of the polarizability and dipole moment, for a series of reactions such as those given in Table I, relative trends in well depths can be predicted. The values for r, the collision diameter, were estimated from van der Waals radii.[13]

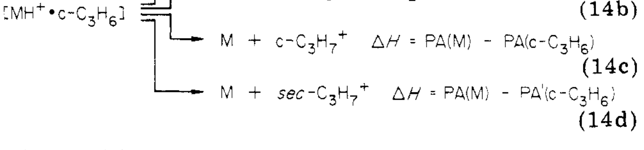
Figure 2 shows the efficiencies of the isotope exchange reactions involving propylene (Table I) as a function of the estimated exothermicity of process 9 or 10. The obvious dependence which exists ties together the approximate correlation with dipole moment of M, mentioned above, and the previously observed correlation[3] with ΔH of the corresponding proton-transfer reaction. Thus, for reactions of approximately constant ΔH, a correlation with well depth W (i.e., with the dipole moment of M) is seen, and for a series of reactions in which the dipole moment of M remains approximately constant, a correlation with the ΔH of the corresponding proton-transfer reaction is observed.

The results shown in Figure 2 indicate that although the overall isotope exchange reactions are thermoneutral, the probability of a reactive collision is dependent on the exothermicity of formation of the [M·sec-$C_3(H,D)_7^+$] intermediate. It has been suggested that such trends in reaction efficiency with ΔH or ΔG of reaction can be explained by the existence of a barrier in the reaction coordinate which diminishes in height as the reaction exothermicity increases.[14] For these thermoneutral isotope exchange processes, such a barrier, if it exists, is not manifested like an energy barrier to the overall reaction, since, in at least two instances, the rate constants for isotope exchange do exhibit negative temperature dependences (Table I and Table III, to be discussed below). Considering mechanism 2, one can derive[4]

$$k/Z = k_c/(k_b + k_c) \qquad (13)$$

The correlation shown in Figure 2 suggests that k_c is dependent on the exothermicity of process 9/10. The negative temperature dependence of the rate constants suggests that in this temperature regime (300–400 K) k_b is comparable in magnitude to k_c and increases with temperature faster than does k_c. If the temperature dependence of k_c is small enough that there is no large change when the temperature is increased from 330 to 403 K, then the observed negative temperature dependence for the (CD_3CDOD^+ + $CH_3CH{=}CH_2$) reactant pair (and the similar negative temperature dependence shown in Table III for reaction with cyclopropane) would indicate that the lifetime of the collision complex decreases by approximately a factor of 2 over this temperature range. Measured temperature dependences of three-body association reactions[15] show approximately the same dependence for reactant species of this complexity.

H/D Exchange Reactions Involving Cyclopropane. Before considering H/D exchange reactions involving cyclopropane, similar to the reactions of propylene discussed above, it is useful to review briefly the various channels which may be open to an (MH^+ + c-C_3D_6) pair (or the analogous pair in which the deuteration is reversed). For greater ease in following the discussion, Figure 3 shows some of the predicted features of the potential surface(s) accessible to such pairs. The greater complexity of these systems is due to the fact that proton-transfer and/or the isotope exchange processes may be envisioned as occurring *without* and *with* ring opening, so that there are four possible exit channels for a [MH^+·c-C_3H_6] complex:



where PA(M) is the proton affinity of M, PA(c-C_3H_6) is the proton affinity of cyclopropane, and PA′(c-C_3H_6) is the apparent proton affinity which would be seen if proton transfer to cyclopropane resulted in the formation of a sec-$C_3H_7^+$ ion product. In the discussion which follows, we take as the heat of formation of c-$C_3H_7^+$ the results of

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[13] A quantum mechanical calculation of the potential surface associated with the [NH_4^+·NH_3] complex (P. Merlet, S. D. Peyerimhoff, and R. J. Buenker, *J. Am. Chem. Soc.*, **94**, 8301 (1972)) predicts an effective collision diameter of about 2.6 × 10^{-8}–2.7 × 10^{-8} cm; since the van der Waals diameter of ammonia is 3.1 × 10^{-8} cm, we have accordingly scaled down all collision diameters estimated from van der Waals radii by a factor of 0.85. All van der Waals diameters were taken from the "Handbook of Chemistry and Physics", R. C. Weast, Ed., 59th ed, CRC Press, Cleveland, 1978–79.

[14] D. K. Bohme, G. I. Mackay, and H. I. Schiff, *J. Chem. Phys.*, 73, 4976 (1980).

[15] D. Smith and N. G. Adams, *Chem. Phys. Lett.* **79**, 563 (1981).

TABLE III: Rate Constants of the Reactions $MH^+ + c\text{-}C_3D_6 \rightarrow MD^+ + C_3D_5H$ and $MD^+ + c\text{-}C_3H_6 \rightarrow MH^+ + C_3H_5D$, and Energetics of Related Processes

			$\Delta H\{M(H,D)^+ + \text{cyclopropane} \rightarrow \text{products}\}$, kcal/mol			
reactants	$10^{10}k$, cm^3/(molecule s)	k/Z[d]	$\rightarrow c\text{-}C_3(H,D)_7^+ + M$[e]	$\rightarrow [M\cdot c\text{-}C_3(H,D)_7^+]$[e,f]	$\rightarrow sec\text{-}C_3(H,D)_7^+ + M$[g]	$\rightarrow [M\cdot sec\text{-}C_3(H,D)_7^+]$[g,h]
$CD_3CND^+ + C_3H_6$	8.1[a]	0.69	+6.7	−18	−1.3	−26
	5.9[b]	0.49				
$C_2H_5CNH^+ + C_3D_6$	5.2[a]	0.48	+10.2	−17	+2.2	−25
$n\text{-}C_3H_7CNH^+ + C_3D_6$	5.2[a]	0.50	+11.5	−13	+3.5	−21
$i\text{-}C_3H_7CNH^+ + C_3D_6$	3.6[a]	0.35	+12.4	−12	+4.4	−20
$CD_3CDOD^+ + C_3H_6$	7.3[a,c]	0.63	+4.8	−16	−3.2	−24
	3.7[b,c]	0.32				
$(HCOOCH_3)H^+ + C_3D_6$	2.8[a]	0.26	+7.9	−9	0	−17
$(HCOOC_2H_5)H^+ + C_3D_6$	1.5[a]	0.15	+11.6	−6	+3.6	−14
$(HCOOCH_2CH_2CH_3)H^+ + C_3D_6$	<0.01[a]	0.0	+12.9	−4	+4.9	−12

[a] 330 K. [b] 398 K. [c] Rate constant for disappearance of CD_3CDOD^+, including both isotope exchange and deuteron-transfer channels. $k(H^+ \text{ transfer}) = (1.7 \pm 0.7) \times 10^{-10}$ cm^3/(molecule s); see Table II. [d] Collision rate constants estimated by using formulations given in ref 11. [e] Taking $\Delta H_f(c\text{-}C_3H_7^+)$ from the theoretical calculation of ref 16 as 8 kcal greater than $\Delta H_f(sec\text{-}C_3H_7^+)$, or 191.1 + 8 = 199 kcal/mol. See footnotes 17 and 18. [f] Enthalpy change for the reaction $M(H,D)^+ + \text{cyclopropane} \rightarrow [M\cdot c\text{-}C_3(H,D)_7^+]$ estimated with eq 12. See footnote 12. For values of r and μ, used, see Table I. [g] $\Delta H_f(sec\text{-}C_3H_7^+)$ taken from ref 18, 191.1 ± 0.7 kcal/mol. [h] Enthalpy change for the process $M(H,D)^+ + \text{cyclopropane} \rightarrow [M\cdot sec\text{-}C_3H_7^+]$ estimated from well depth of complex relative to separated $sec\text{-}C_3H_7^+ + M$ reactants and endothermicity of proton transfer to give $sec\text{-}C_3H_7^+$ ionic product.

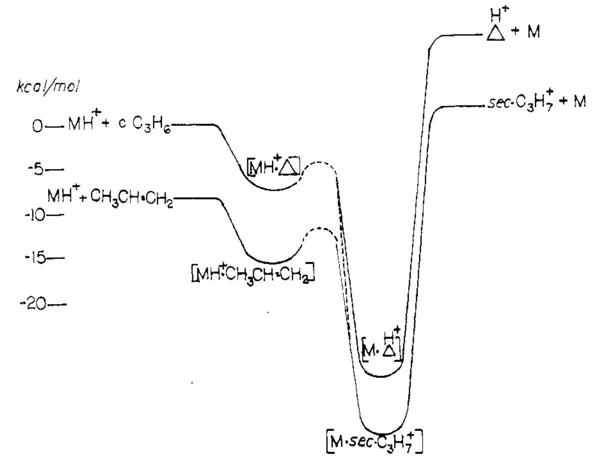

Figure 3. Cross section of potential surfaces available to $MH^+ + c\text{-}C_3H_6$ reactants showing typical relative energy levels for M compounds studied here for $\{MH^+ + c\text{-}C_3H_6\}$, $\{MH^+ + CH_3CH{=}CH_2\}$, $\{c\text{-}C_3H_7^+ + M\}$, $\{sec\text{-}C_3H_7^+ + M\}$, and the corresponding intermediate complexes. The $\{MH^+ + c\text{-}C_3H_6\}$ and $\{MH^+ + CH_3CH{=}CH_2\}$ energy levels differ by 7.8 kcal/mol; the $\{c\text{-}C_3H_7^+ + M\}$ and $\{sec\text{-}C_3H_7^+ + M\}$ energy levels are assumed (ref 17) to differ by ~8 kcal/mol.

a theoretical calculation,[16] which predicts that $\Delta H_f(c\text{-}C_3H_7^+)$ is greater than $\Delta H_f(sec\text{-}C_3H_7^+)$ by ~8 kcal/mol.[17] On this basis, the proton affinity of cyclopropane would be 179 kcal/mol if a protonated cyclopropane ion were formed in the proton-transfer reaction. If proton transfer to cyclopropane results in the formation of a $sec\text{-}C_3H_7^+$ product ion, the apparent proton affinity is 187 kcal/mol.[18]

Table II shows the results of several auxiliary experiments which were performed in an attempt to check if proton transfer to cyclopropane does lead to a $sec\text{-}C_3H_7^+$ product

$$MH^+ + c\text{-}C_3H_6 \rightarrow sec\text{-}C_3H_7^+ + M \qquad (15)$$

when the proton donor has a proton affinity greater than ~179 kcal/mol and less than 187 kcal/mol. The results (Table II) show that when M has a proton affinity lower than approximately 178 kcal/mol, proton transfer to form a $C_3H_7^+$ product of undefined structure occurs at the collision rate. Proton donors having proton affinities between 178 and 186 kcal/mol do react by proton transfer to $c\text{-}C_3H_6$ but with rate constants which are lower than the collision rate constant. In every case in which $C_3H_7^+$ is formed, it is seen to undergo proton transfer to M, as it should if it has the $sec\text{-}C_3H_7^+$ structure.

Table III gives rate constants and reaction efficiencies for isotope exchange reactions involving cyclopropane:

$$MD^+ + c\text{-}C_3H_6 \rightarrow MH^+ + C_3H_5D \qquad (16)$$

$$MH^+ + c\text{-}C_3D_6 \rightarrow MD^+ + C_3D_5H \qquad (17)$$

Estimated endothermicities for proton (deuteron) transfer to form $C_3(H,D)_7^+$ products are also given. It can be seen that for three of the reactant pairs in Table III (reactions of $HCOOCH_3{\cdot}H^+$, CD_3CND^+, and CD_3CDOD^+) proton or deuteron transfer to give a $sec\text{-}C_3H_7^+$ product is actually thermoneutral or exothermic. In these cases, experiments were performed to see if proton transfer was indeed occurring. In the case of $HCOOCH_3$–$c\text{-}C_3H_6$ and CD_3CN–$c\text{-}C_3D_6$ mixtures, neither the $HCOOCH_3{\cdot}H^+$ nor the CD_3CND^+ ion showed any evidence of undergoing proton transfer. These two ions showed no decay where $C_3(H,D)_7^+$ was continuously ejected from the system in these mixtures, and, in neither case, could any propyl ions be observed. The CH_3CHOH^+ ion, however, does transfer a proton to cyclopropane to form a $C_3H_7^+$ product, which, in turn reacts rapidly with CH_3CHO. As shown in Tables II and III, the probability that a CH_3CHOH^+–$c\text{-}C_3H_6$ collision results in proton transfer

$$CH_3CHOH^+ + c\text{-}C_3H_6 \rightarrow sec\text{-}C_3H_7^+ + CH_3CHO \qquad \Delta H = -3.1 \text{ kcal/mol} \qquad (18)$$

is about 0.15, while about half of the collisions between

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(16) K. Raghavachari, R. A. Whiteside, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 5649 (1981).

(17) An experimental determination of the proton affinity of cyclopropane has been reported (S.-L. Chong and J. L. Franklin, *J. Am. Chem. Soc.*, **94**, 6347 (1972)) and agrees very well with that predicted from the theoretical value for the heat of formation of $c\text{-}C_3H_7^+$ used here. Although one cannot a priori rule out the possibility that ring opening occurred in the proton-transfer equilibria involving cyclopropane, the agreement with the recent theoretical calculation as well as the implications of the results reported here would indicate that ring opening was not a problem in that study.

(18) The heat of formation of $sec\text{-}C_3H_7^+$ is taken to be 191.1 ± 0.7 kcal/mol (from H. M. Rosenstock, R. Buff, M. A. A. Ferreira, S. G. Lias, A. C. Parr, R. L. Stockbauer, and J. L. Holmes, *J. Am. Chem. Soc.*, accepted for publication). The heat of formation of cyclopropane is 12.73 ± 0.14 kcal/mol and that of propylene is 4.88 ± 0.16 kcal/mol, both from J. B. Pedley and J. Rylance, "N. P. L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds", University of Sussex, 1977.

TABLE IV: Isotope Exchange Ratios, k_{24}/k_{23}, for Reactions with Partially Deuterated Propylenes and Cyclopropane

initial reactant ion	$CD_3CH{=}CH_2$	$CH_3CH{=}CD_2$	$CH_3CH{=}CHD$	$c\text{-}1,1\text{-}C_3H_4D_2$
CD_3CND^+		0.45		0.49
$C_2H_5CNH^+$	1.06	0.53	0.25	0.50
$n\text{-}C_3H_7CNH^+$	1.15			0.48
$i\text{-}C_3H_7CNH^+$	1.16			0.43
CD_3CDOD^+	1.75	0.75	0.33	0.63
$(HCOOCH_3)H^+$	1.53	0.59	0.29	0.45
$(HCOOC_2H_5)H^+$	1.25	0.61	0.27	0.51
predicted				
complete scrambling	1.00	0.50	0.20	0.20
mechanism A[a]	1.50	0.67	0.25	
mechanism B[b]	1.50	0.67	1.00	0.50

[a] Mechanism A: H^+ or D^+ transferred to $C(H,D)_2$ group forming a sec-$C_3(H,D)_7^+$ in the complex. Return transfer may involve either methyl group of the sec-$C_3(H,D)_7^+$ species. [b] Mechanism B: H^+ or D^+ transferred to $C(H,D)_2$ group and return transfer involves the same $C(H,D)_3$ group. Accuracy, ±10%.

CD_3CDOD^+ and c-C_3H_6 result in the occurrence of the isotope exchange process

$$CD_3CDOD^+ + c\text{-}C_3H_6 \rightarrow CD_3CDOH^+ + C_3H_5D \qquad (19)$$

which would be thermoneutral if C_3H_5D were cyclopropane, and 7.8 kcal/mol exothermic if the neutral product is propylene.[18]

In Figure 2, we showed that for propylene reactant molecules, there is a correlation between the probability for isotope exchange and the exothermicity of formation of the complex in which proton transfer has occurred, [M·sec-$C_3(H,D)_7^+$]. An analogous plot for cyclopropane reactants is also shown in Figure 2, where the efficiencies of isotope exchange are related to the estimated exothermicities associated with the processes

$$MD^+ + c\text{-}C_3H_6 \rightarrow [MD^+{\cdot}c\text{-}C_3H_6] \rightarrow [M{\cdot}c\text{-}C_3H_6D^+] \qquad (20)$$

$$MH^+ + c\text{-}C_3D_6 \rightarrow [MH^+{\cdot}c\text{-}C_3D_6] \rightarrow [M{\cdot}c\text{-}C_3D_6H^+] \qquad (21)$$

Again, an obvious correlation exists, which shows that when the exothermicity of process 20/21 is close to zero (actually, ~4 kcal/mol on this plot, but it must be remembered that there are large uncertainties associated with the estimation of the well depths of ion–molecule complexes), the probability for the occurrence of isotope exchange is zero. The plots for cyclopropane and for propylene reactants appear to be almost superimposed on one another. If instead of process 20/21, we were to assume that isotope exchange with a cyclopropane reactant involved the formation of a [M·sec-$C_3(H,D)_7^+$] complex, e.g.

$$MH^+ + c\text{-}C_3H_6 \rightarrow [MD^+{\cdot}c\text{-}C_3H_6] \rightarrow [M{\cdot}sec\text{-}C_3H_6D^+] \qquad (22)$$

then the points in Figure 2 relating to the cyclopropane results would be shifted to reflect the greater exothermicity (by ~8 kcal/mol) of processes such as 22 over processes 20/21, and the probability for isotope exchange would appear to reach zero when the associated process (e.g., process 22) is still clearly exothermic (by ~12 kcal/mol). This suggests that the isotope exchange does involve formation of [M·c-$C_3(H,D)_7^+$] complexes, and that [M·sec-$C_3(H,D)_7^+$ complexes cannot be formed in these systems without going through a [M·c-$C_3(H,D)_7^+$] intermediate. One reaches the same conclusion through an examination of the results given in Table II, where it is seen that, in proton transfer to cyclopropane, there is a low probability for formation of separated (M + sec-$C_3H_7^+$) products, even when that channel is strongly exothermic.

Isotope Exchange Involving Partially Deuterated Propylene and Cyclopropane. More detailed information about the mechanism of the isotope exchange processes involving propylene and cyclopropane can be obtained from an examination of such processes in partially labeled molecules.

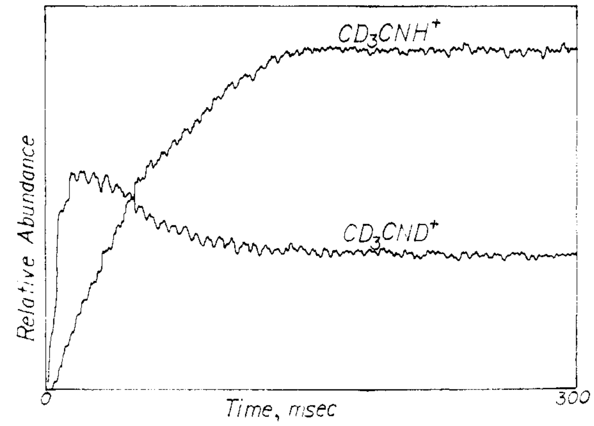


Figure 4. CD_3CND^+ and CD_3CNH^+ in a CD_3CN–$CH_3CH{=}CD_2$ (4.4:1) mixture as a function of time.

In the case of propylene, Table IV presents results for reactions of a series of proton (deuteron) donors with $CD_3CH{=}CH_2$, $CH_3CH{=}CD_2$, and $CH_3CH{=}CHD$. In these systems, the initial reactant ion, MD^+ for example, undergoes an isotope exchange:

$$MD^+ + CD_3CH{=}CH_2 \rightarrow MH^+ + C_3D_4H_2 \qquad (23a)$$

$$MD^+ + CH_3CH{=}CD_2 \rightarrow MH^+ + C_3D_3H_3 \qquad (23b)$$

$$MD^+ + CH_3CH{=}CHD \rightarrow MH^+ + C_3D_2H_4 \qquad (23c)$$

In such experiments, the product MH^+ ions will also react with propylene:

$$MH^+ + CD_3CH{=}CH_2 \rightarrow MD^+ + C_3D_2H_4 \qquad (24a)$$

$$MH^+ + CH_3CH{=}CD_2 \rightarrow MD^+ + C_3DH_5 \qquad (24b)$$

$$MH^+ + CH_3CH{=}CHD \rightarrow MD^+ + C_3H_6 \qquad (24c)$$

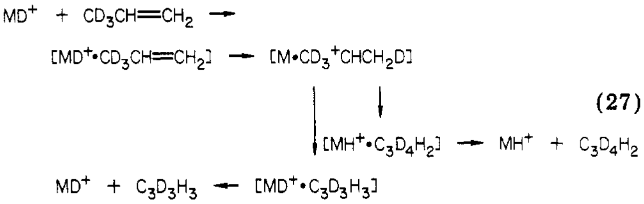
At long times, a constant ratio of MD^+ to MH^+ is observed, as shown in Figure 4 for the CD_3CND^+ and CD_3CNH^+ ions observed in a CD_3CN–$CH_3CH{=}CD_2$ (4.4:1) mixture. The ratio of the ions MD^+/MH^+ observed at long times represents the ratio k_{24}/k_{23} for a particular partially deuterated propylene. These experiments can give meaningful results only if there is no isotope effect operating on the exchange reaction. It was demonstrated that such isotope effects are small; in a CD_3CN–$CD_3CD{=}CD_2$–$CH_3CH{=}CH_2$ (1:0.72:0.72) mixture, the ratio of the ions CD_3CND^+–CD_3CNH^+ resulting from the occurrence of reactions 25 and 26 was 0.93 at long times.

$$CD_3CND^+ + CH_3CH{=}CH_2 \rightarrow CD_3CNH^+ + C_3H_5D \qquad (25)$$

$$CD_3CNH^+ + CD_3CD{=}CD_2 \rightarrow CD_3CND^+ + C_3D_5H \qquad (26)$$

The results given in Table IV show the relative importances of reactions 23 and 24 for the partially deuterated propylenes $CD_3CH{=}CH_2$, $CH_3CH{=}CD_2$, and $CH_3CH{=}CHD$. In the case of $CD_3CH{=}CH_2$ reactant (reactions 23a and 24a), the ratio k_{24}/k_{23} is unity when M is a nitrile, 1.7 when M is an aldehyde, and ~1.4 when M is a formate. The results obtained for the nitriles are just what one would predict if there is a statistical probability of recovering an H or a D atom from the propyl ions formed in the complexes $[RCN{\cdot}C_3H_3D_4^+]$ and $[RCN{\cdot}C_3H_4D_3^+]$. Reactions of protonated (deuterated) nitriles with $CH_3CH{=}CD_2$ similarly lead to an observed ratio for k_{24}/k_{23} which is in agreement with that predicted assuming complete scrambling of H and D atoms on the $C_3(H,D)_7^+$ species in the complex.

Protonated aldehyde or formate reactants, however, exhibit much different relative rate constants for reactions 23 and 24 than would be predicted by assuming statistical scrambling in the complex. The results obtained in these systems can best be rationalized by noting that the observed ratios for k_{24}/k_{23} are in fairly good agreement in every case with the ratios which would be predicted if we assumed that the proton (deuteron) was transferred to the methylene group of the propylene molecule, that no scrambling occurred, and that the proton (deuteron) which was returned to the M species in the complex came from either one of the two methyl groups of the *sec*-$C_3(H,D)_7^+$. For example



(27)

The differences in the degree of scrambling observed in the complex when M is a nitrile, or when M is one of the other compounds studied here, can be understood in terms of the model described above. That is, the relatively deeper well depths associated with $[RCN{\cdot}C_3H_7^+]$ complexes (Table I) will cause these complexes to be longer lived than corresponding formate complexes (i.e., the greater well depth will influence k_c and k_d in mechanism 2), and thus permit the occurrence of more scrambling. On the other hand, the well depths for the acetaldehyde complexes are comparable to those for the nitrile complexes, yet results obtained in acetaldehyde–propylene mixtures (Table IV) show significantly less scrambling than is observed in the nitrile complexes. It has been shown that isomerization processes occurring in an ion–molecule complex are facilitated by the presence of a molecule having a high dipole moment.[19] . These results indicate that scrambling of H(D) atoms in the complex may also be facilitated when the M species in the complex has a high dipole moment.

Table IV also includes some results on the relative probabilities of reactions involving partially deuterated cyclopropane, c-1,1-$C_3H_4D_2$:

$$MD^+ + c\text{-}C_3H_4D_2 \rightarrow MH^+ + C_3H_3D_3 \qquad (23d)$$

$$MH^+ + c\text{-}C_3H_4D_2 \rightarrow MD^+ + C_3H_5D \qquad (24d)$$

The results for reactions involving protonated nitriles or formates agree very well with the predictions of a model in which the $H(D)^+$ is transferred to a particular $C(H,D)_2$ group in the molecule, and the return transfer involves the same C atom and affiliated H(D) species. (The corner-protonated structure is predicted to be the most stable structure for c-$C_3H_7^+$.)[16] The reactions involving protonated (deuterated) acetaldehyde, however, match the predictions of a model which assumes that a propyl ion is formed in the complex; in this case, proton transfer to form the propyl ion does occur. These results suggest that, except when proton transfer to give a *sec*-$C_3H_7^+$ product ion actually occurs, the H/D transfer reactions involving cyclopropane do not involve a [M·*sec*-$C_3(H,D)_7^+$] intermediate. That is, for most of the reactions considered here, the results indicate that ring opening in the complex does not occur. This is in agreement with the conclusion reached above.

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(19) S. G. Lias, D. M. Shold, and P. Ausloos, *J. Am. Chem. Soc.*, **102**, 2540 (1980).