minescence intensity. To produce a change similar to that observed, it is necessary to change the average transfer rate  $W^{(mc)}$  by as much as a factor of 5.

# V. Summary

Previous work established that the phosphorescence spectrum of 4-bromo-4'-chlorobenzophenone doped into polystyrene films is a superpositin of a cluster spectrum and a discrete molecular spectrum. Building on those observations, we have studied spectral diffusion in this system. The motivation for these studies is the interest in energy-transfer processes in molecular aggregates. It was found that when the film containing the aggregates was illuminated by laser light at wavelengths equal to or longer than 4172 Å, phosphorescence of discrete molecules was observed. The discrete molecules were excited by energy transfer from molecules in clusters. The transfer rate was found to depend strongly on the excitation energy was attributed to a correlation between the excitation energy and the location of molecules within the cluster. This correlation results from the differences in the moleculemolecule and molecule–polymer interactions. Excitation at different energies therefore excites molecules at different positions in a cluster. At the highest excitation energies delocalized aggregate states (DAS), associated with the interior regions of the clusters, are excited. These states relax by rapidly transferring enegy to localized aggregate states (LAS) associated with the boundary regions of the aggregate. The LAS at lower energies can be excited directly, and these states transfer energy efficiently to discrete molecules outside the cluster. Time-resolved phosphorescence spectra and time evolution measurements showed that the time scale for energy transfer from clusters to discrete molecules is in the range of 100–400  $\mu$ s, which is faster than the unimolecular decay of a discrete BCBP molecule, which is 2.8 ms, but slower than the time for intracluster energy transfer, which is <20  $\mu$ s.

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Registry No. BCBP, 27428-57-5; polystyrene, 9003-53-6.

# Alkyl-Transfer Reactions between Protonated Alcohols and Ethers. Gas-Phase Alkylation of Formaldehyde

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Alkyl-transfer reactions involving protonated alcohols and ethers, of the general type  $R_2OR'^+ + R''_2O \rightarrow R''OR'^+ + R_2O$ , may be classified according to the degree of alkylation, i.e., the total number n of alkyl groups in the system. For systems containing two alkyl groups, the reaction is alkyl transfer between protonated and neutral alcohols,  $ROH_2^+ + ROH \rightarrow R_2OH^+$ + H<sub>2</sub>O, and we measured rate constants for R = Me, Et, *i*-Pr, and *t*-Bu. The rate constants are  $(0.6-1.5) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> when R is a normal alkane and  $(6 \pm 1) \times 10^{-10}$  when R = *i*-Pr and *t*-Bu. The larger rate constants in the latter may be due to a lowered barrier for the initial partial R<sup>+</sup>-OH<sub>2</sub> bond dissociation. For reaction systems containing three alkyl groups, i.e., the reactions of protonated ethers  $R_2OH^+$  with alcohols R'OH, the possible channels are alkyl transfer from the alcohol, yielding  $R_2OR'^+$ , or alkyl transfer from the ether, yielding  $ROR'H^+$ . Both processes are observed in  $(CH_3)_2OH^+ + C_2D_5OH^$ which yields both  $(CH_3)_2OC_2D_5H^+$  and  $CH_3OC_2D_5H^+$ . For systems containing four alkyl groups an example is the reaction  $(CH_3)_2OH^+ + (CH_3)_2O \rightarrow (CH_3)_3O^+ + CH_3OH$ , which is a slow reaction with  $k < 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Finally, for the highest possible degree of alkylation, n = 5, an example is methyl transfer in  $(CH_3)_2OCD_3^+ + (CH_3)_2O \rightarrow (CH_3)_2OCH_3^+ + CH_3OCD_3$ which is a very slow reaction, observed only above 500 K. The rate constants for alcohols show negligible temperature dependence between 300 and 670 K, but in the most highly alkylated system the rate increases strongly with temperature, and an activation energy of 15 kcal mol<sup>-1</sup> is observed. The results show that alkyl transfer occurs in systems with all possible degrees of alkylation, but the rates tend to decrease with increasing alkylation. In addition to saturated systems, alkyl transfer is also observed with unsaturated ions or neutrals. Examples are alkyl transfer between unsaturated oxocarbonium ions  $C_2H_3O^+$  and methanol and ethanol and between protonated alcohols and CH<sub>2</sub>O. These reactions have rate constants of  $(1-4) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Depending on the temperature coefficients, the alkylation of formaldehyde may be important in astrochemical synthesis.

#### Introduction

Alkyl-transfer reactions involving saturated oxygen compounds, i.e., water, alcohols, and ethers, can be written in general as

$$R_2 O R'^+ + R''_2 O \to R''_2 O R'^+ + R_2 O$$
(1)

For a systematic treatment, these reactions may be classified according to the total number n of alkyl groups in the system. The present work will deal with reaction systems with all possible degrees of alkylation with n = 2-5. The possible reactions in these systems vary with n, and therefore we shall survey briefly the various possible reactions.

First, for completeness sake, it should be noted that systems with n < 2 are also possible. For n = 0 reaction 1 consists of proton transfer between H<sub>3</sub>O<sup>+</sup> and H<sub>2</sub>O and their deuteriated variants.

For n = 1, an example would be alkyl transfer from  $ROH_2^+$  to  $D_2O$ , whose products are equivalent, however, to the products of hydrogen scrambling. These reactions are outside the scope of the present work.

For n = 2, the reaction is the well-known self-alkylation of protonted alcohols which produces protonated ethers:<sup>1-3</sup>

$$ROH_2^+ + ROH \rightarrow R_2OH^+ + H_2O$$
(2)

The reaction was shown<sup>4a</sup> to be a backside  $SN_2$  reaction, but the mechanism is dependent on ion energy.<sup>4b</sup> Of the possible types

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<sup>(2)</sup> Henis, J. M. S. J. Am. Chem. Soc. 1968, 90, 844.

<sup>(3) (</sup>a) Beauchamp, J. L.; Caserio, M. J. J. Am. Chem. Soc. 1972, 94, 2638.
(b) Beauchamp, J. L.; Caserio, M. J.; McMahon, T. B. J. Am. Chem. Soc. 1974, 96, 6243.

<sup>(4) (</sup>a) Kleingeld, J. C.; Nibbering, N. M. M. Org. Mass Spectrom. 1982, 17, 136. (b) Russell, D., personal communication.

of reaction systems with various degrees of alkylation surveyed here, only these reactions have been investigated extensively.1-4

$$R_2OH^+ + ROH \rightarrow R_3O^+ + H_2O$$
(3)

Alternatively, alkyl transfer from the protonated ether could occur:

$$R_2OH^+ + R'OH \rightarrow RORH'^+ + ROH$$
(4)

Of course, the reaction will lead to a new product only if R and R' are different.

For n = 4, reaction between protonated and neutral ethers, if alkyl transfer occurs, it will produce a tertiary oxonium ion:

$$R_2OH^+ + R_2O \rightarrow R_3O^+ + ROH$$
 (5)

Finally, for the highest degree of alkylation, n = 5, the possible reaction consists of an exchange of alkyl groups between an alkylated and a neutral ether molecule:

$$R_{3}O^{+} + R'_{2}O \rightarrow R'_{2}OR^{+} + R_{2}O$$
 (6)

The objective of the present paper is to demonstrate that alkyl-transfer reactions occur for reactants with all degrees of alkylation, from n = 2 to 5. We shall present rate constants for several of the reactions, to investigate the effects of the number and size of the alkyl groups on the reaction kinetics.

Alkyl-transfer reactions are also of interest when the receptors are molecules other than alcohols or ethers. For example, we observed recently alkyl-transfer reactions from protonated alcohols, ROH<sub>2</sub><sup>+</sup>, to nitriles, RCN.<sup>5,6</sup> In the case of HCN, these reactions were shown to produce protonated isocyanides, RNCH+:

$$ROH_2^+ + HCN \rightarrow RNCH^+ + H_2O \tag{7}$$

To generalize the range of alkyl-transfer reactions between oxygen compounds, we shall observe some systems where the ionic alkyl donor, or the neutral alkyl acceptor, is unsaturated. Reactions of unsaturated ions involve the oxocarbonium ions  $CH_2OCH_3^+$  and  $CH_3CH_2OC_2H_5^+$ . Reactions of an unsaturated neutral will be shown by alkyl transfer from protonated alcohols to H<sub>2</sub>CO:

$$ROH_2^+ + H_2CO \rightarrow H_2COR^+ + H_2O \tag{8}$$

This reaction may be of interest in planetary or interstellar synthesis, since formaldehyde is present in many such environments.

### **Experimental Section**

The work was carried out on the pulsed NBS ion cyclotron resonance (ICR) mass spectrometer<sup>7</sup> and on the NBS pulsed high-pressure mass spectrometer.8 The instruments and experimental procedures were described in detail previously.<sup>7,8</sup>

In most of the systems studied, several parallel and consecutive reactions can occur. ICR double resonance (DR) was applied to elucidate reactant-product relationships. In most cases, double resonance showed a negative response; i.e., the signal intensty due to a product ion decreased when the precursor ion was ejected. In several cases, double resonance showed a positive responsive; i.e., the product ion intensity showed an increase when the reactant was ejected. In addition, in some cases a "double-winged" behavior at or near the precursor's ejection frequency was observed. In the double-winged cases the product ion intensity increased at both sides of the precursor frequency but decreased at the exact ejection frequency. This type of behavior was dealt with in detail by Goode





Figure 1. Time profiles of ions in a reaction system of  $1.45 \times 10^{-6}$  Torr of CH<sub>3</sub>OH and  $0.5 \times 10^{-7}$  Torr of C<sub>2</sub>D<sub>5</sub>OH.

et al., who showed that the decrease of product ion intensity may be due to the ejection of the precursor, a decrease of the rate constant with ion energy, or detuning due to changes in spacecharge effects.<sup>9</sup> Although this double-winged behavior may be due to instrumental artifacts, in most of the cases observed by Goode et al. it was associated with cases where k in fact increases with ion energy. Similarly, an increase in product ion intensity upon double-resonance excitation of the precursor usually results from an increase in k with ion energy. Therefore, in the present case we interpret both as evidence for an endothermic reaction or one with an activation barrier.

Our ICR conditions involve pressures of 10<sup>-5</sup>-10<sup>-6</sup> Torr and trapping times up to 500 ms. These conditions allow from tens to hundreds of ion-neutral collisions. In contrast, the pulsed high-pressure mass spectrometer allows thousands of collisions, and we used this technique for very slow reactions. Moreover, pulsed high-pressure mass spectrometry allows measurements over a wide temperature range, and we used it to measure rate constants above 600 K.

# Results

A Sample Reaction System Containing Methanol and Ethanol. From reactions 2-4 it is evident that ions of considerable complexity and reactions with a high degrees of alkylation can build up from alcohols. This is illustrated by a reaction system containing CH<sub>3</sub>OH and C<sub>2</sub>D<sub>5</sub>OH.

The time profiles of the major ions in a mixture of methanol and  $C_2D_5OH$  are shown in Figure 1. The reactions in this system were elucidated from the time profiles and confirmed by double-resonance (DR) techniques. The possible proton- and alkyl-transfer reactions are summarized in eq 9-16.

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \qquad (9)$$

$$CH_{3}OH_{2}^{+} + C_{2}D_{5}OH - C_{2}D_{5}OH_{2}^{+} + CH_{3}OH$$
(10)

$$(CH_3OC_2U_5)H + H_2O$$
 (11)

(12)

$$C_2D_5OH_2^+ + C_2D_2OH \rightarrow (C_2D_5)_2OH^+ + H_2O$$
 (12)  
 $C_2D_5OH_2^+ + CH_3OH \rightarrow (CH_3OC_2D_5)H^+ + H_2O$  (13)

$$(CH_3)_2OH^+ + C_2D_5OH \longrightarrow (CH_3OC_2D_5)H^+ + CH_3OH (14)$$

$$(CH_3)_2OCH_3^+ + C_2D_5OH \not \rightarrow (CH_3)_2OC_2D_5^+ + CH_3OH$$
(16)

In terms of extent of alkylation, reactions 9-13 are examples of n = 2, reactions 14 and 15 are examples of n = 3, and reaction 16 is an example for n = 4. Of the possible reactions 9–16, we

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TABLE I: Rate Constants and Thermochemistry for Alkyl-Transfer Reactions

reaction	k <sup>a</sup>	<i>T</i> , K	−∆H° <sup>b</sup>	$D^{\circ}(R^+-OR_2')$
$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O$	$10.8 \pm 2.2^{d}$	340	15	68
	$6.0 \pm 2$	570-670		
$C_2H_5OH_2^+ + C_2H_5OH \rightarrow (C_2H_5)_2OH^+ + H_2O$	6.8 ± 1.1	340	18	37
	$4 \pm 1$	640-670		
$n-C_3H_7OH_2^+ + n-C_3H_7OH \rightarrow (n-C_3H_7)_2OH^+ + H_2O$	$10.3 \pm 1.2$	340	18	35
$i-C_3H_7OH_2^+ + i-C_3H_7OH \rightarrow (i-C_3H_7)_2OH^+ + H_2O$	$61.4 \pm 1.2$	340	18	24
$n - C_4 H_9 O H_2^+ + n - C_4 H_9 O H \rightarrow (n - C_4 H_9)_2 O H^+ + H_2 O$	$15.3 \pm 2.0$	340	19	32
$t - C_4 H_9 O H_2^+ + t - C_4 H_9 O H \rightarrow (t - C_4 H_9)_2 O H^+ + H_2 O$	$66 \pm 10$	340		11
$(CH_3)_2OH^+ + (CH_3)_2O  ((CH_3)_2O)_2H^+$	$1.2 \pm 0.3$	340	_	
$(CH_3)_2OH \rightarrow (CH_3)_3O^+ + CH_3OH$			9	84
$(CH_3)_2OCD_3^+ + (CH_3)_2O \rightarrow (CH_3)_2OCH_3^+ + (CH_3)OCD_3$	0.00054	544	0	94
	0.00380	648		
	0.0062	482		
$(CH_3)_2OCH_3^+ + 0 \longrightarrow 0 - CH_3^+ + (CH_3)_2O$	0.022	668		
Unsaturated Systems				
$CH_{2}OH_{2}^{+} + H_{2}CO \rightarrow CH_{2}OCH_{2}^{+} + H_{2}O$	$2.1 \pm 0.1$	340		68
$C_1H_2OH_2^+ + H_2OO \rightarrow C_2H_2OCH_2^+ + H_2O$	$1.7 \pm 0.3$	340		37
$i_{1}C_{1}H_{1}OH_{1}^{+} + H_{2}CO \rightarrow i_{2}C_{1}H_{2}OCH_{1}^{+} + H_{2}O$	$4.3 \pm 1.0$	340		24
$CH_{3}OCH_{3}^{+} + (CH_{3})_{2}O \rightarrow (CH_{3})_{3}O^{+} + CH_{3}OH$	$2.6 \pm 0.3$	340		
$CH_{3}CHOH^{+} + C_{2}H_{5}OH \rightarrow CH_{3}CHOC_{2}H_{5}^{+} + H_{2}O$	9 ± 2	640-670		
Clustering Reaction				

 $(CH_3)_2OH^+ + 2(CH_3)_2O \rightarrow ((CH_3)_2O)H^+ + (CH_3)_2O \qquad 1 \times 10^{-22 c}$ 

<sup>*a*</sup> Units of  $10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Error estimate ±20%. <sup>*b*</sup> In kcal mol<sup>-1</sup>, based on data from ref 13 and 14. <sup>*c*</sup> In cm<sup>6</sup> s<sup>-1</sup>. <sup>*d*</sup> Literature values:  $1.0 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> for the methanol reaction and  $2.2 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> for the ethanol reaction, all from ref 1.

actually observed all but (11) and (16). Reaction 11 does not occur because fast exothermic proton transfer (10) is preferred with these reactants. Reaction 16, with the highest degree of alkylation, may be too slow to observe under our ICR conditions. Double resonance showed that reaction 14, which also has a high degree of alkylation, probably has an activation barrier, since it showed a double-winged response. The alternative reaction (15) between the same reactants was also observed to proceed slowly.

In summary, this reaction system demonstrates the complexity of ionic reactions in the presence of only two alcohols and illustrates a variety of reactions with n = 2 and 3.

Kinetics of Alkyl-Transfer Reactions in Saturated Systems. In neat alcohols, the protonated molecule reacts with a neutral alcohol molecule through one of the following channels:

$$ROH_2^+ + ROH \rightarrow R_2OH^+ + H_2O$$
(17)

$$\rightarrow (\text{ROH})_2 \text{H}^+ \tag{18}$$

$$\rightarrow (ROOR)H^+ + H_2 \tag{19}$$

The rate constants of reactions of this type in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol, have been measured in the present work, as shown in Table I. On the whole, our results are in good agreement with earlier measurements of these rates.<sup>1-3</sup>

Reaction 18 is a clustering reaction which usually involves a three-body mechanism and negative temperature coefficient.<sup>10</sup> With larger reactants it may involve second-order kinetics with radiative stabilization or a combination of these mechanisms. Reaction 19 involves extensive rearrangement and may well involve an activation barrier. The relative rates of reactions 17–19 should be therefore strongly dependent on conditions. Our general observation was that the contribution from channel 18 increases with the alcohol size in accordance with the expected mechanism.

In the higher alcohols, especially the branched ones (2-propanol and 2-methyl-2-propanol), protonation may lead to loss of water and formation of a stable carbonium ion. This results in a low steady-state signal of these protonated alcohols and introduces a larger error in the rate constant measurement in these systems. An interesting question is whether alkyl transfer in the  $n-C_3H_7OH$ and  $n-C_4H_9OH$  systems also involves rearrangement to the more stable  $i-C_3H_7^+$  and  $t-C_4H_9^+$  structures, so that the products are  $n-C_3H_7O-i-C_3H_7H^+$  and  $n-C_4H_9O-t-C_4H_9H^+$ , respectively. This would be similar to the results of Lias et al.,<sup>11,12</sup> who demonstrated the rearrangements of  $C_4H_9^+$  isomers to the  $t-C_4H_9^+$  structure in ion-molecule complexes.

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To extend kinetic measurements to systems with a higher degree of alkylation, we measured the rate constant for reaction 20, a system with n = 4.

$$(CH_3)_2OH^+ + (CH_3)_2O - (CH_3)_3O^+ + CH_3OH (20)$$
  
 $((CH_3)_2O)_2H^+ (21)$ 

Reaction 20 appears to involve some activation barrier. This is concluded by an increase in the m/z 61 ion signal as the double-resonance oscillator energizes the m/z 47 precursor ion. Under our conditions, reaction 20 proceeds, though slowly, and reaction 21 also occurs. As seen in Table I, the overall reaction (20) and (21) is slow. However, the clustering reaction (21) is slow because of the low pressure in the system. Pressure studies showed that it is largely a third-order reaction under these conditions, and therefore the distribution of the products is pressure-dependent. The rate constant for the clustering reaction was  $1 \times 10^{-22}$  cm<sup>6</sup> s<sup>-1</sup>, an extremely fast reaction for third-order clustering. This is consistent with exceptionally large rate constants observed by McEwan in similar clustering reactions of polar molecules such as CH<sub>3</sub>CN when the third body is the same polar molecule.<sup>15</sup>

To further extend quantitative kinetic studies, we also measured the rate constant for two reactions with the highest possible degree of alkylation, n = 5, in reaction 22. For this purpose, we generated the  $(CH_3)_2OCD_3^+$  ion in a reaction system of  $(CH_3)_2O$  in  $CD_3Cl$ in the NBS pulsed high-pressure mass spectrometer. The thermoneutral alkyl-exchange reaction (22) is then observed.

$$(CH_3)_2OCD_3^+ + (CH_3)_2O \rightarrow (CH_3)_2OCH_3^+ + CH_3OCD_3$$
(22)

The rate constant was measured at high temperatures. The rate constant is very slow, and it increases with temperature, from

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<sup>(15)</sup> McEwan, M. J., private communication, 1988.

 $k(544) = 5.4 \times 10^{-15}$  cm<sup>3</sup> s<sup>-1</sup> to  $k(648) = 3.8 \times 10^{-14}$  cm<sup>3</sup> s<sup>-1</sup>. Another reaction of the same order, n = 5, counting the cycloalkyl group as two substituents, is

$$(CH_3)_2OCH_3^+ + \bigcirc - \bigcirc -CH_3^+ + (CH_3)_2O$$
 (23)

This reaction is exothermic by  $4 \pm 2$  kcal mol<sup>-1</sup> according to our equilibrium results, and it is faster by a factor of 18 at 540 K than the thermoneutral reaction (22) (Table I).

Temperature Coefficients. For a fuller understanding of alkyl-transfer reactions, temperature coefficients are needed. So far, rate constants have been published only at 300 K. In the present work, we used the high-pressure mass spectrometer to obtain rate constants at elevated temperatures. Unfortunately, the temperature range of these measurements is small, since protonated alcohols cluster strongly below 550 K. However, a significant temperature range is covered by combining the ICR and high-pressure results.

For reaction 9, i.e., the condensation of methanol, we obtained rate constants between 570 and 670 K. The results give  $k = (6 \pm 2) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> and show no significant temperature dependence in this range. This value can be compared with (10.8  $\pm 2.2$ )  $\times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> at 340 K. For reaction 12, the condensation of ethanol, we obtain  $(4 \pm 1) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> between 640 and 670 K, which may be compared with (6.8  $\pm 1.1$ )  $\times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> at 340 K. Considering the use of different techniques at low and high temperatures and the combined estimated error limits, the results show that both reactions have negligible, or at most slightly negative, temperature coefficients that may be expressed approximately as  $k = CT^{-0.7}$  to  $CT^{-1}$ .

In contrast, in the most highly alkylated systems strongly positive temperature coefficients are observed. For reaction 22, which is a thermoneutral methyl-transfer process, the results give  $E_a = 13.4$  kcal mol<sup>-1</sup>, the highest measured for any ion-molecule reaction. The intercept gives  $1.2 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>, corresponding to about the collision rate. This suggests that the slow rate is due entirely to the activation barrier. For reaction 23, which is similar to (22) in the degree of alkylation but is exothermic by 4 kcal mol<sup>-1</sup>, the activation energy is 5.1 kcal mol<sup>-1</sup>, significantly smaller than that of the thermoneutral reaction (22). Here the Arrhenius plot gives an intercept lower than the collision rate,  $1.1 \times 10^{-11}$ cm<sup>3</sup> s<sup>-1</sup>. This may be due to a steric factor of error.

Alkyl Transfer in Unsaturated Oxygen Compounds. In the reaction systems above, we observed that alkyl transfer occurs in saturated oxygen compounds and ions with all possible degrees of alkylation. To further generalize alkyl-transfer reactions in oxygen compounds, we shall present here examples of alkyl transfer where the ionic or neutral component is unsaturated.

We observed that protonated alcohols may alkylate formaldehyde and form ions of the type  $ROCH_2^+$ . The time profiles of the major ions in a mixture of methanol and formaldehyde are shown in Figure 2. This system shows examples of reactions with both unsaturated ions and neutrals. The principal reactions observed are the following:

$$H_2COH^+ + CH_3OH \rightarrow CH_3OH_2^+ + H_2CO$$
 (24)

$$CH_{3}OH_{2}^{+} + CH_{3}OH \rightarrow (CH_{3})_{2}OH^{+} + H_{2}O \qquad (9)$$

$$CH_3OH_2^+ + H_2CO \rightarrow CH_3OCH_2^+ + H_2O \qquad (25)$$

$$CH_3OCH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2CO \quad (26)$$

The reaction of primary interest is the formation of  $H_2COCH_3^+$  ions in reaction 25. We observed that the ion can then further react to alkylate CH<sub>3</sub>OH in reaction 26. Reactions 25 and 26 constitute a catalytic cycle equivalent to reaction 9.

Reactions analogous to (25) are the alkylation of  $H_2CO$  by other protonated alcohols, and we report the rate constants for  $C_2H_5OH_2^+$  and i- $C_3H_7OH_2^+$  in Table I. These observations suggest that the alkylation of  $H_2CO$  by alcohols may be common.

The reactant in reaction 26 is the oxocarbonium ion  $CH_2OCH_3^+$ . This unsaturated species may be seen as alkylated



**Figure 2.** Time profiles of ions in a reaction system of  $1.2 \times 10^{-6}$  Torr of CH<sub>2</sub>O and  $6 \times 10^{7}$  Torr of CH<sub>3</sub>OH. Note that the total ion intensity decreases with time due to ion losses.

 $CH_2CO$ . The reaction showed a positive double-resonance response, which suggests that it has as activation barrier. An analogous reaction is the condensation reaction

$$C_2H_5O^+ + C_2H_5OH \rightarrow C_2H_3OC_2H_5^+ + H_2O$$
 (27)

We observed this reaction in the pulsed high-pressure mass spectrometer, between 640 and 670 K. The reaction system was  $C_2H_5OH$  in  $CH_4$ , and  $C_2H_5O^+$  was formed by the decomposition of  $C_2H_5OH_2^+$  at these high temperatures. In this case the ion may be  $CH_3CHOH^+$ , which is the most stable isomer. The reaction is then probably the alkylation of the ion by  $C_2H_5$  transfer from the neutral alcohol. The rate constant,  $9 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>, is in the same range as the other alkyl-transfer reactions.

Reactions 26 and 27 involve unsaturated systems with two alkyl groups. A system with higher degree of alkylation is reaction 28. We observed this reaction under ICR conditions, in  $(CH_3)_2O$ , where  $CH_2OCH_3^+$  is generated as a fragment ion.

$$CH_{3}OCH_{2}^{+} + (CH_{3})_{2}O \rightarrow (CH_{3})_{3}O^{+} + H_{2}CO$$
 (28)

## Discussion

Relation between Rate Constants and  $O-R^+$  Bond Dissociation Energies. The present results show that alkyl-transfer reactions are common in ionic systems. Alkyl-transfer reactions can occur in reaction systems with any degree of alkylation, as long as faster processes such as proton transfer are endothermic and therefore do not compete.

For a more detailed understanding, we can now examine the kinetic effects of the alkyl groups and the degree of alkylation.

The results in Table I show that rate constants for alkyl transfer involving alcohols tend to be faster with increasing size and branching of the transferred alkyl group. This does not result from variation in the reaction exothermicities, which are comparable for all the alcohols. Unfortunately, the thermochemistry for the t-C<sub>4</sub>H<sub>9</sub>OH system is not known, but the trends for the other alcohols suggest that the exothermicity for this system is also similar. Interestingly, however, the reactions in the i-C<sub>3</sub>H<sub>7</sub>OH and t-C<sub>4</sub>H<sub>9</sub>OH systems are substantially faster than the CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH systems.

A possible reason for the observed trend may be related to the energy of partial dissociation of the  $R^+$ -OH<sub>2</sub> bonds in the course of the transfer process. The importance of the R-X bond dissociation step is demonstrated by recent observations on protonated amines.<sup>16,17</sup> For example, an energized C<sub>2</sub>H<sub>5</sub>(*i*-C<sub>3</sub>H<sub>7</sub>)NH<sub>2</sub><sup>+</sup> ion can be formed by reaction or IR irradiation. This ion dissociates

<sup>(16)</sup> Moylan, C. R.; Brauman, J. I. J. Am. Chem. Soc. 1985, 107, 761.

<sup>(17)</sup> Ausloos, P.; Lias, S. G. J. Am. Chem. Soc., in press.

predominantly to form  $C_2H_5NH_3^+ + C_3H_6$ , although forming *i*- $C_3H_7NH_2^+ + C_2H_4$  would be more exothermic. The controlling step is the intracomplex dissociation of the excited  $C_2H_5(i-C_3H_7)NH_2^+$  ion by alkyl elimination, where the weaker bond to *i*- $C_3H_7^+$  is favored.

Similarly, a rate-controlling factor in the alkyl-transfer reactions from alcohols may be the partial  $R^+$ -OH<sub>2</sub> dissociation reactions. For all of the alcohol-alcohol reactions, except methanol in Table I, k increases as  $D(H_2O-R^+)$  decreases. In fact, the data for the ethyl, n-propyl, isopropyl, and n-butyl alcohols yield a linear correlation:

$$\ln k = C - 0.17D(R^+ - OH_2)$$
(29)

The correlation suggests that an increase of 1 kcal mol<sup>-1</sup> in  $D(R-OH_2^+)$  increases the activation energy for the alkyl-transfer reaction by 0.1 kcal mol<sup>-1</sup>.

Based on the correlation, methyl transfer is faster by about a factor of 30 than expected, and *tert*-butyl transfer is slower by about a factor of 10 than expected. Both deviations are consistent, at least qualitatively, with steric effects.

The ordering of the rate constants for the three alcohol-formaldehyde reactions in Table I is similar to that in the corresponding alcohol-alcohol reactions. Of course, these reactions too involve the same partial  $R^+$ -OH<sub>2</sub> dissociation in the course of the reaction.

The effects of the degree of alkylation can be examined by comparing methyl-transfer kinetics in three reactions:  $CH_3OH_2^+$ +  $CH_3OH$ , and  $(CH_3)_2OH^+$  and  $(CH_3)OCH_3^+$  with  $(CH_3)_2O$ . The reactions become markedly slower with increasing degree of alkylation, and the third reaction is not observable at 300 K. In these reactions the dissociating bonds are  $H_2O-CH_3^+$ ,  $CH_3$ - $(H)O-CH_3^+$ , and  $(CH_3)_2O-CH_3^+$ , and the bond dissociation energies are 68, 84, and 94 kcal mol<sup>-1</sup>, respectively. Therefore, in this series too an inverse correlation is observed between bond dissociation energy and rate constant.

In a classic investigation, Kebarle et al. showed that methyl transfer from halonium ions to alkylbenzenes involves a double-well potential surface with central barriers that may be lower or higher than the energy of the reactants and, correspondingly, may have negative or positive temperature coefficients.<sup>18</sup> In analogy, the present observations would be consistent with a double-well surface with a central barrier whose height increases with increasing  $R_2O-R^+$  dissociation energy.

In analogy with Kebarle's results,<sup>18</sup> some of the present reactions may have negative, zero, or positive temperature coefficients, depending of the height of the energy barrier. As we noted, for CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH no significant temperature coefficient or a slightly negative temperature coefficient is noted. Therefore, the top of the central energy barrier may be close to or slightly below the energy of the reactants. Also, most of the reactions in Table I, and especially the alkylation of H<sub>2</sub>CO, exhibit normal, negative double resonance. This suggests that these reactions do not have a barrier higher than the energy of the reactants and,

(18) Sharma, D. K.; Kebarle, P. J. Am. Chem. Soc. 1982, 104, 19.

in analogy to Kebarle's results, may have negative temperature coefficients.<sup>18</sup> In contrast, the system with the highest alkylation,  $(CH_3)_2OCD_3^+ + (CH_3)_2O$ , showed substantial activation energy, and positive or double-winged double-resonance behavior in several cases quoted above also indicates an energy barrier.

The reaction system of CH<sub>3</sub>OH and C<sub>2</sub>D<sub>5</sub>OH demonstrated that ion-molecule reactions, starting from alcohols, can build up ions with higher degrees of alkylation. In particular, we noted reactions leading to protonated symmetric and asymmetric ethers, in this case  $(CH_3)_2OH^+$ ,  $CH_3OC_2D_5H^+$ , and  $(C_2D_5)_2OH^+$ .

Synthesis by Alkyl Transfer and Possible Roles in Astrochemistry. Generally, in a mixture of two alcohols, the mixed protonated ether is formed. In mixtures of methanol with ethanol, 2-propanol, and 2-methyl-2-propanol, alkyl transfer from the higher protonated alcohol to methanol is exothermic by  $12 \pm 1$ kcal mol<sup>-1,13,14</sup> The product asymmetric ether ions can react further by alkyl transfer to form the higher dialkyl protonated ether. For example, in a mixture of methanol and 2-methyl-2propanol, we observed the reaction

$$(t-C_4H_9OCH_3)H^+ + t-C_4H_9OH \rightarrow (t-C_4H_9)_2OH^+ + CH_3OH$$
(30)

This reaction, and the analogous reactions involving ethanol and 2-propanol in mixtures with methanol, are all exothermic by the same amount,  $5 \pm 1$  kcal mol<sup>-1</sup>. Therefore, a series of alkyl-transfer reactions in mixtures of ethanol with higher alcohols lead to the protonated symmetric higher ether as the ultimate product. In astronomical environments such as planetary atmospheres these product ethers can recombine with an electron or become deprotonated to yield the neutral asymmetric or higher symmetric ethers.

As we saw, in the presence of  $H_2CO$ , the protonated alcohols transfer an alkyl group form  $ROCH_2^+$  ions. Upon recombination, these may form products such as R, RO,  $CH_2$ , or CH + Hradicals, while recombination of  $ROH_2^+$  will probably form mostly ROH. Therefore, alkylation of the ubiquitous  $H_2CO$  molecule can have a significant effect on the overall chemistry.

The alkylation reactions can be significant in the interstellar environment only if they proceed at significant rates. We note that the rate constants for these reactions in Table I are lower by factors of 10–100 than the usual collision rates of about  $10^{-9}$ cm<sup>3</sup> s<sup>-1</sup>. However, these reactions exhibit normal negative double-resonance responses, which may indicate negative temperature coefficients, as is observed for many exothermic ion-molecule reactions. This could make the reactions proceed at significant rates under low-temperature space conditions. For example, a relatively small negative temperature coefficient of  $k = AT^{-2}$  could make the reactions in Table I proceed at unit efficiency below 50 K. The temperature and energy dependence of alkyl-transfer reactions should be therefore further studied.

**Registry No.** CH<sub>3</sub>OH, 67-56-1; C<sub>2</sub>H<sub>5</sub>OH, 64-17-5; *n*-C<sub>3</sub>H<sub>7</sub>OH, 71-23-8; *i*-C<sub>3</sub>H<sub>7</sub>OH, 67-63-0; *n*-C<sub>4</sub>H<sub>9</sub>OH, 71-36-3; *t*-C<sub>4</sub>H<sub>9</sub>OH, 75-65-0; (CH<sub>3</sub>)<sub>2</sub>O, 115-10-6; (CH<sub>3</sub>)<sub>2</sub>OCH<sub>3</sub><sup>+</sup>, 43625-65-6; H<sub>2</sub>CO, 50-00-0; tetra-hydrofuran, 109-99-9.