Rate Constants and Product Branching Fractions for the Reactions of H_3O^+ and NO^+ with C_2-C_{12} Alkanes

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Gas-phase ion molecule reactions of H_3O^+ and NO^+ with a number of C_2-C_{12} alkanes have been studied using a variable temperature-selected ion flow tube instrument. Reaction rate constants and product branching fractions were measured at 300 K, and temperature dependences of the rate constants and product branching fractions for reactions of C_7 and C_8 alkanes were examined from 300 to 500 K. The threshold size for H_3O^+ reaction occurs at hexane, with the reaction rate constants increasing steadily with alkane size. Association is the predominant reaction channel at 300 K for C_3-C_{12} alkanes, although these products thermally dissociate back into initial reactants between 300 and 400 K. The proton-transfer reaction channel is expected to be exothermic for large alkanes; however, this reaction channel does not proceed at the collision rate, nor are any direct proton-transfer product ions observed. The presence of smaller alkyl product ions suggests proton-transfer product ions may dissociate into smaller alkyl fragment ions and neutral alkanes. The threshold size for NO^+ reaction with *n*-alkanes also occurs at hexane, and the reaction proceeds primarily via hydride transfer as previous experiments have indicated. However, a number of smaller product ions are also observed for the reactions of NO^+ with all *n*-alkanes larger than butane, with the branching fraction of the nonhydride transfer product ions increasing with increasing alkane size. Together with our previously reported results regarding the reactions of various atmospheric ions with octane isomers, the present results indicate that H_3O^+, NO^+, and O_2^+ are not suitable chemical ionization agents for analysis of hydrocarbon emissions.

Introduction

Introducing trace amounts of various compounds into hydrocarbon fuels can dramatically affect the rate of combustion.[1] Certain additives act as accelerants by facilitating the formation of critical free radicals, while other additives have a retarding effect. We have undertaken a comprehensive laboratory study of the reactions of air plasma ions with a variety of alkanes, especially the larger alkanes commonly found in fuels such as gasoline or kerosene, to explore the possibility that air plasma ions could be used as additives to enhance the rate of combustion of hydrocarbon fuels or to reduce the ignition delay time.

Previously, we have reported temperature-dependent rate constants and product branching ratios for the reactions of NO^+, O_2^+, O^+, N^+, and N_2^+ with octane and isooctane (2,2,4-trimethylpentane).[2] We have also reported on the competition between hydrogen abstraction and reactive detachment in the reactions of O^- with various C_2-C_{12} alkanes.[3] We have continued the survey and in this paper report the kinetics of H_3O^+ and NO^+ reacting with a variety of alkanes. Specifically, we report rate constants measured at 300 K for the reactions of H_3O^+ with C_2H_6, C_3H_8, C_4H_{10}, iso-C_4H_{10}, C_6H_{14}, C_7H_{16}, C_8H_{18}, iso-C_8H_{18}, and $C_{10}H_{22}$. Product branching fractions were determined for all reactions except C_2H_6 as well as for the reaction of H_3O^+ with $C_{12}H_{26}$. The temperature dependences of the rate constants and product branching fractions for the reactions of C_7 and C_8 alkanes were examined from 300 to 500 K. We also report rate constants measured at 300 K for the reactions of NO^+ with C_4H_{10}, iso-C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, iso-C_8H_{18}, and $C_{10}H_{22}$. Product branching fractions were determined for all reactions except that of $C_{10}H_{22}$. As with the H_3O^+ reactions, the temperature dependences of the rate constants and product branching fractions for the reactions of NO^+ with C_7 and C_8 alkanes were examined from 300 to 500 K.

The rate constants and product branching ratios we have measured for the reactions of air plasma ions with various alkanes are being incorporated into detailed hydrocarbon combustion kinetic models formulated by Lindstedt and Maurice[4] in order to evaluate further the effects on combustion of ion−hydrocarbon reactions. Preliminary modeling results[5] suggest that ions may indeed act as “additives,” enhancing combustion by decreasing ignition delay times.

Although the focus of our laboratory survey of air plasma ions reacting with hydrocarbon fuels has been on exploring the role that ion−molecule reactions may play in enhancing rates of combustion, the H_3O^+ and NO^+ rate constants and product branching fractions reported here are also pertinent to trace gas analysis of hydrocarbon emissions via chemical ionization. Several instruments have been developed which utilize reactions of H_3O^+, O_2^+, or NO^+ to detect trace organic compounds in air and breath samples,[6−9] and the recent application of such instruments for analysis of hydrocarbon emissions will be discussed in light of the present results.

Experimental Section

The measurements were made using the Air Force Research Laboratory variable temperature-selected ion flow tube.[10] Instruments of this type have been the subject of review,[11] and

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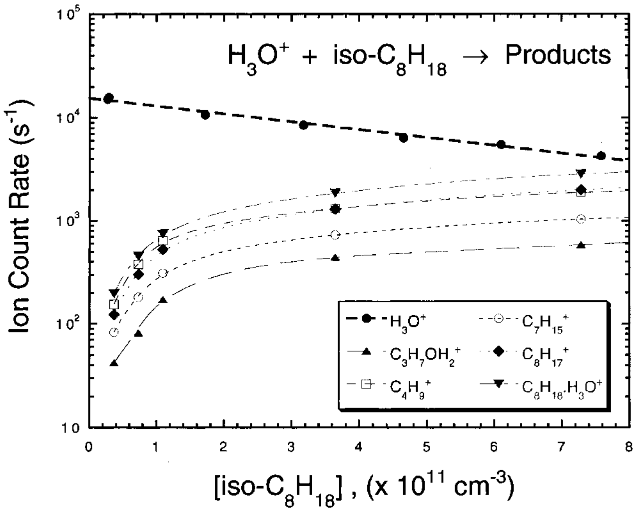

Figure 1. Example of measurements taken using the SIFT instrument. Typical decay plot, for the reaction of H_3O^+ with iso-C_8H_{18}, from which rate constants and product branching fractions are extracted.

only those aspects relevant to the present study will be discussed in detail. The reactant ions were produced in a moderate pressure ion source (0.1−1 Torr) by electron impact on H_2O or NO, mass selected in a quadrupole mass filter, and injected into the flow tube through a Venturi inlet. The neutral reactants were introduced downstream through a finger inlet, a 1/8 in. stainless steel tubing which enters the flow tube perpendicular to the flow and terminates at the radial center of the flow tube. The reactant neutral gas reacted with the ion for a known reaction time (∼2 ms) in a fast flow of He buffer gas (∼100 m s^{-1}), maintained at a total pressure of ∼0.45 Torr. A small fraction of the gas in the tube flowed through a sampling orifice, and the reactant and product ions in this flow were mass analyzed in a second quadrupole mass filter and detected by a particle multiplier. Reaction times were determined from previous time-of-flight measurements. Rate constants were extracted from least-squares fits of the logarithm of the reactant ion signal versus concentration of reactant neutral. An example of the measurements taken for the reactions of H_3O^+ with iso-C_8H_{18} is shown in Figure 1. Rate constants could not be determined accurately for $C_{12}H_{26}$ because of the difficulties in working with a compound of such low vapor pressure. The accuracy of the measured overall rate constants is ±25%, and the relative accuracy is ±15%.[10]

Product branching fractions were derived in the normal fashion by recording the product ion count rates as a function of the neutral reactant flow rate. To account for the effects of secondary reactions between the product ions and the reactant neutral, the reported branching fractions were determined by extrapolating the measured branching percentages to a neutral reactant flow rate of zero. Small signal levels and a myriad of products with nearly equal mass prevented branching fractions for the reactions of NO^+ with $C_{12}H_{26}$ and $C_{10}H_{22}$ from being measured accurately. We could determine that the products were of the same type as for the smaller alkanes but could not accurately determine the branching fractions.

The reactants were obtained commercially: C_2H_6 (Scientific Gases, 99.2%), *n*-C_3H_8 (Scientific Gases, 99.0%), *n*-C_4H_{10} (Aldrich, 98%), iso-C_4H_{10} (Aldrich, 99%), *n*-C_5H_{12} (Aldrich, 99^+%), *n*-C_6H_{14} (Aldrich, 99^+%), *n*-C_7H_{16} (Aldrich, 99% anhydrous), *n*-C_8H_{18} (Aldrich, 99^+% anhydrous), iso-C_8H_{18} (Aldrich, 99.8% anhydrous), *n*-$C_{10}H_{22}$ (Aldrich, 99^+% anhydrous), and *n*-$C_{12}H_{26}$ (Aldrich, 99% anhydrous). The maximum water content of the anhydrous samples was <0.005%. The reactants were used without further purification except for repeated freeze/thaw cycles to eliminate trapped vapors. The He buffer gas (99.999%) was passed through a molecular sieve trap to reduce residual water vapor. Precursor gases used in the source were NO for forming NO^+ ions and H_2O for forming H_3O^+ ions. The formation of electronically excited NO^+ reactant ions was monitored by introducing a small flow of N_2 into the flow tube, prior to introducing any hydrocarbon reactants. Because only the excited electronic state of NO^+ charge transfers to N_2, it was possible to monitor the formation of N_2^+ and then vary source conditions until <2% of the reactant ions were being formed as NO^{+*}. Vibrationally excited states of the reactant ion, NO^+ ($\nu > 0$), were quenched prior to reaction by introducing a small flow of N_2 into the tube upstream of the reaction zone.

Results and Discussion

Overall reaction rate constants (k_2) and reaction efficiencies (k_2/k_c) are presented in Table 1 for the reactions of H_3O^+ with C_2H_6, C_3H_8, C_4H_{10}, iso-C_4H_{10}, C_6H_{14}, C_7H_{16}, C_8H_{18}, iso-C_8H_{18}, and $C_{10}H_{22}$. Results are presented in Table 2 for the reactions of NO^+ with C_4H_{10}, iso-C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, iso-C_8H_{18}, and $C_{10}H_{22}$. All reactions were studied at 300 K, and the reactions with C_7 and C_8 compounds were also studied at 400 and 500 K. Product ion branching fractions were determined for nearly all the reactions cited above. In addition, the reaction of H_3O^+ with $C_{12}H_{26}$ was studied at 300 K, and the branching fraction data are presented in Table 1. Tables 1 and 2 indicate the detected ion products with the assumed neutrals, the branching fractions, and the enthalpy change for each reaction channel. For the H_3O^+ reactions, the rate constants for individual reaction channels (obtained by multiplying the channel's branching fraction by the overall reaction rate constant) are also indicated in Table 1. It should be noted that branching fractions of one or two percent could result from impurities, and may not be significant; however, 1−2% product fractions were included in the tables because (a) in some cases these products became more abundant as the temperature was varied, and (b) in some cases there were several different product ions at the 1−2% level, the sum of which exceeded the maximum level of impurities.

Standard reaction enthalpies, $\Delta H°$ at 298 K, presented in Tables 1 and 2 were calculated using the following assumptions: (1) reactions of H_3O^+ and NO^+ with *n*-alkanes produce straight-chain ion and neutral products, (2) reactions of H_3O^+ and NO^+ with branched alkanes produce branched ion and neutral products, and (3) the formation of secondary carbocation products is favored over that of primary carbocations because of their energetic stability. Reported thermochemistry is taken from the compilations of Lias et al.[12] and Hunter et al.[13] except as follows. $\Delta H°_f$ for the larger $C_nH_{2n+1}^+$ straight-chain cations, $C_8H_{17}^+$, $C_9H_{19}^+$, and $C_{10}H_{21}^+$, were estimated to be 645, 615, and 585 kJ mol^{-1}, respectively, utilizing an empirical equation of the form $\Delta H°_f (M^+) = A - Bn + C/n$, where n is the total number of atoms in the molecule and A, B, and C are constants derived from the data of structurally similar, although smaller, straight-chain alkyl cations ($C_3H_7^+$−$C_7H_{13}^+$). Models such as this have been used successfully in the past to estimate ion enthalpies of formation for compounds within a homologous series.[12] Estimated $\Delta H°_f$ for large protonated alkane species, $C_nH_{2n+3}^+$, were also obtained, using a similar formula based on data obtained from small protonated alkanes (CH_5^+−$C_3H_9^+$). However, the resulting estimates for $\Delta H°_f$ [$C_nH_{2n+3}^+$] are

TABLE 1: Reaction Rate Constants and Product Branching Fractions Measured for the Reactions of H_3O^+ with a Variety of Alkanes

	$\Delta H°$	300 K	400 K	500 K
$H_3O^+ + C_2H_6 \rightarrow$ products		*<0.0001 (<0.01)*		
$H_3O^+ + n\text{-}C_3H_8 \rightarrow$ products		*0.00030 (0.02)*		
$C_3H_8H_3O^+$		[1.0]		
$H_3O^+ + n\text{-}C_4H_{10} \rightarrow$ products		*0.0016 (0.1)*		
$C_4H_{10}H_3O^+$		[1.0]		
$H_3O^+ + \text{iso-}C_4H_{10} \rightarrow$ products		*0.0018 (0.1)*		
$C_4H_9^+ + H_2 + H_2O$	−5			
$H_3O^+ + n\text{-}C_6H_{14} \rightarrow$ products		*0.030 (1.0)*		
$C_6H_{14}H_3O^+$		0.019 [0.63]		
$C_6H_{13}^+ + H_2 + H_2O$	+38	0.0060 [0.20]		
$C_4H_9^+ + C_2H_6 + H_2O$	+16	0.0012 [0.04]		
$C_4H_9OH_2^+ + C_2H_6$	−87	0.00090 [0.03]		
$C_3H_7OH_2^+ + C_3H_8$	−71	0.0030 [0.10]		
$H_3O^+ + n\text{-}C_7H_{16} \rightarrow$ products		*0.26 (12)*	*0.079 (4.0)*	*0.074 (3.0)*
$C_7H_{16}H_3O^+$		0.20 [0.77]		
$C_7H_{15}^+ + H_2 + H_2O$	+33	0.013 [0.05]	0.0095 [0.12]	
$C_6H_{13}^+ + CH_4 + H_2O$	−16		0.0016 [0.02]	
$C_5H_{11}^+ + C_2H_6 + H_2O$	+3	0.013 [0.05]	0.021 [0.26]	0.020 [0.27]
$C_4H_9^+ + C_3H_8 + H_2O$	+16	0.018 [0.07]	0.039 [0.49]	0.043 [0.58]
$C_4H_9OH_2^+ + C_3H_8$	−87	0.010 [0.04]		
$C_3H_7^+ + C_4H_{10} + H_2O$	+27		0.0047 [0.06]	0.011 [0.15]
$C_3H_7OH_2^+ + C_4H_{10}$	−73	0.0052 [0.02]	0.0040 [0.05]	
$H_3O^+ + n\text{-}C_8H_{18} \rightarrow$ products		*0.58 (25)*	*0.18 (8.0)*	*0.19 (8.0)*
$C_8H_{18}H_3O^+$		0.37 [0.63]		
$C_8H_{17}^+ + H_2 + H_2O$	+23	0.017 [0.03]	0.0072 [0.04]	
$C_6H_{13}^+ + C_2H_6 + H_2O$	−4	0.035 [0.06]	0.041 [0.23]	0.029 [0.15]
$C_5H_{11}^+ + C_3H_8 + H_2O$	+3	0.093 [0.16]	0.059 [0.33]	0.080 [0.42]
$C_4H_9^+ + C_4H_{10} + H_2O$	+15	0.041 [0.07]	0.058 [0.32]	0.067 [0.35]
$C_4H_9OH_2^+ + C_4H_{10}$	−88	0.029 [0.05]		
$C_3H_7^+ + C_5H_{12} + H_2O$	+28		0.014 [0.08]	0.015 [0.08]
$H_3O^+ + \text{iso-}C_8H_{18} \rightarrow$ products		*0.49 (21)*	*0.26 (11)*	*0.27 (12)*
$C_8H_{18}H_3O^+$		0.16 [0.32]		
$C_8H_{17}^+ + H_2 + H_2O$	−36	0.11 [0.22]	0.044 [0.17]	
$C_7H_{15}^+ + CH_4 + H_2O$	−48	0.064 [0.13]	0.039 [0.15]	0.0081 [0.03]
$C_5H_{11}^+ + C_3H_8 + H_2O$	+96			0.0054 [0.02]
$C_4H_9^+ + C_4H_{10} + H_2O$	−36	0.13 [0.27]	0.15 [0.57]	0.23 [0.85]
$C_3H_7^+ + C_5H_{12} + H_2O$	+37		0.013 [0.05]	0.027 [0.10]
$C_3H_7OH_2^+ + C_5H_{12}$	−63	0.029 [0.06]	0.016 [0.06]	
$H_3O^+ + n\text{-}C_{10}H_{22} \rightarrow$ products		*0.99 (40)*		
$C_{10}H_{22}H_3O^+$		0.47 [0.47]		
$C_{10}H_{21}^+ + H_2 + H_2O$	+2	0.020 [0.02]		
$C_8H_{17}^+ + C_2H_6 + H_2O$	−22	0.020 [0.02]		
$C_7H_{15}^+ + C_3H_8 + H_2O$	−10	0.069 [0.07]		
$C_6H_{13}^+ + C_4H_{10} + H_2O$	−6	0.18 [0.18]		
$C_5H_{11}^+ + C_5H_{12} + H_2O$	+2	0.15 [0.15]		
$C_4H_9^+ + C_6H_{14} + H_2O$	+16	0.079 [0.08]		
$H_3O^+ + n\text{-}C_{12}H_{26} \rightarrow$ products		- -		
$C_{12}H_{26}H_3O^+$		[0.58]		
$C_9H_{19}^+ + C_3H_8 + H_2O$	−31	[0.03]		
$C_8H_{17}^+ + C_4H_{10} + H_2O$	−23	[0.09]		
$C_7H_{15}^+ + C_5H_{12} + H_2O$	−10	[0.11]		
$C_6H_{13}^+ + C_6H_{14} + H_2O$	−5	[0.10]		
$C_5H_{11}^+ + C_7H_{16} + H_2O$	+3	[0.07]		
$C_4H_9^+ + C_8H_{18} + H_2O$	+16	[0.02]		

[a] Listed in italic type are the overall rate constants (k_2) given in units of 10^{-9} cm^3 s^{-1} and the reaction efficiency (k_2/k_c) given in percent and shown in parentheses. For each alkane, the detected-ion-product channels are listed with the assumed neutrals. Standard reaction enthalpies (298 K), given in kJ mol^{-1}, were calculated as described in the text. Rate constants for each individual reaction channel are given in units of 10^{-9} cm^3 s^{-1}. Branching fractions are shown in brackets.

deemed less reliable than the previously described estimates for $\Delta H°_f$ [$C_nH_{2n+1}^+$] because they require a longer extrapolation from known data. Finally, $\Delta H°_f$ for $(CH_3)_3CCH_2C(CH_3)_2^+$ was estimated to be 559 kJ mol^{-1} by assuming this quantity equals $\Delta H°_f$ [$CH_3(CH_2)_4C(CH_3)_2^+$] + $\Delta H°_f$ [$(CH_3)_3CCH_2CH(CH_3)_2$] − $\Delta H°_f$ [$CH_3(CH_2)_4CH(CH_3)_2$].

H_3O^+ + Alkanes. H_3O^+ reacts with many organic compounds via proton transfer. When the proton affinity (PA) of H_2O is greater than the PA of the organic compound, the proton-transfer reaction is exothermic and often proceeds at or near the collision rate.[14] As shown in Figure 2, the PA of small alkanes (methane, ethane, propane, and isobutane) are known to be less than that of water.[13] Thus, proton-transfer reactions with H_3O^+ and these small alkanes are endothermic and are expected to be slow, as was observed. A previous determination of the rate constant for the proton-transfer reaction of H_3O^+ with isobutane indicated the reaction was nearly collisional,[15] compared with a 0.1% reaction efficiency for butane measured in the present work. We observe no difference in the overall reaction efficiencies for butane and isobutane. Since the reaction is endothermic we feel that the present value for isobutane is correct. For the larger alkanes, the PA's have not been measured

TABLE 2: Reaction Rate Constants and Product Branching Fractions Measured for the Reactions of NO^+ with a Variety of Alkanes

	$\Delta H°$	300 K	400 K	500 K
$NO^+ + n\text{-}C_4H_{10} \rightarrow$ products		*0.0025 (0.3)*		
$C_4H_9^+ + HNO$	+8	1.0		
$NO^+ + \text{iso-}C_4H_{10} \rightarrow$ products		*0.90 (59)*		
$C_4H_9^+ + HNO$	+16	1.0		
$NO^+ + n\text{-}C_5H_{12} \rightarrow$ products		*0.0039 (0.2)*		
$C_5H_{11}^+ + HNO$	−6	0.91		
$C_3H_7NOH^+ + C_2H_4$		0.02		
$C_4H_9^+ + CH_3NO$	−228	0.03		
$C_2H_5NOH^+ + C_3H_6$		0.04		
$NO^+ + n\text{-}C_6H_{14} \rightarrow$ products		*0.028 (2)*		
$C_6H_{13}^+ + HNO$	−14	0.83		
$C_3H_7NOH^+ + C_3H_6$		0.12		
$C_2H_5NOH^+ + C_4H_8$		0.05		
$NO^+ + n\text{-}C_7H_{16} \rightarrow$ products		*0.083 (5)*	*0.088 (5)*	*0.097 (6)*
$C_7H_{15}^+ + HNO$	−19	0.65	0.64	0.10
$C_4H_9NOH^+ + C_3H_6$		0.15	0.05	0.01
$C_5H_{11}^+ + NH_3 + CH_2CO$	−159		0.05	0.03
$C_3H_7NOH^+ + C_4H_8$		0.14		
$C_4H_9^+ + NH_3 + CH_3CHCO$	−182	0.04	0.24	0.81
$C_2H_5NOH^+ + C_5H_{10}$		0.02		
$C_3H_7^+ + NH_3 + C_2H_5CHCO$	−179		0.02	0.02
$NO^+ + n\text{-}C_8H_{18} \rightarrow$ products		*0.54 (28)*	*0.42 (22)*	*0.42 (22)*
$C_8H_{17}^+ + HNO$	−30	0.62	0.63	0.03
$C_5H_{11}NOH^+ + C_3H_6$		0.09	0.03	0.01
$C_6H_{13}^+ + NH_3 + CH_2CO$	−166			0.03
$C_4H_9NOH^+ + C_4H_8$		0.18	0.05	0.02
$C_5H_{11}^- + NH_3 + CH_3CHCO$	−115	0.03	0.15	0.56
$C_3H_7NOH^+ + C_5H_{10}$		0.08	0.04	
$C_4H_9^- + NH_3 + C_2H_5CHCO$	−108		0.10	0.30
$C_3H_7^+ + CH_3NH_2 + CH_3CHCO$	−105			0.05
$NO^+ + \text{iso-}C_8H_{18} \rightarrow$ products		*1.8 (95)*	*1.9 (100)*	*1.9 (100)*
$C_8H_{17}^+ + HNO$	−86	0.93	0.32	
$C_4H_9^+ + C_4H_8 + HNO$		0.07	0.68	1.0
$NO^+ + n\text{-}C_{10}H_{22} \rightarrow$ products		*1.2 (59)*		

[a] Listed in italic type are the overall rate constants (k_2) given in units of 10^{-9} cm^3 s^{-1} and the reaction efficiency (k_2/k_c) given in percent and shown in parentheses. For each alkane, the detected ion product channels are listed with the assumed neutrals and the branching fractions. Standard reaction enthalpies (298 K), given in kJ mol^{-1}, were calculated as described in the text.

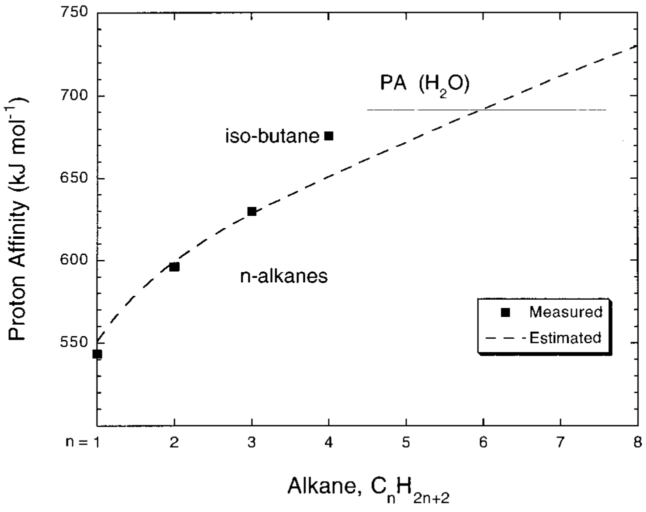

Figure 2. The proton affinity of methane, ethane, propane, and isobutane compared to that of H_2O. All values taken from refs 12,13. Proton affinity values for larger *n*-alkanes were estimated as described in the text and are shown as the dashed curve.

previously. However, within a homologous series such as the *n*-alkanes, the PA is expected to increase with size, which suggests the proton-transfer reaction may become exothermic at some larger size. Estimates for the larger alkane PA's can be obtained by using known thermochemistry for C_nH_{2n+2} and H^+ and estimated enthalpies of formation for $C_nH_{2n+3}^+$ (described above) in determining $\Delta H°$ for the reaction

$$C_nH_{2n+2} + H^+ \rightarrow C_nH_{2n+3}^+ \quad \Delta H° = -\text{PA} \tag{1}$$

Proton affinities for the larger *n*-alkanes, calculated from eq 1, are shown as a dashed curve in Figure 2. Based on these estimates, the PA's of *n*-alkanes become greater than that of water near hexane. (It is interesting to note that the PA estimates indicate hexane is as basic as water in the gas phase.)

Although the proton-transfer reactions should be exothermic for the larger alkanes included in this study, the reactions do not proceed at or near the collision value (in contrast to many exothermic proton-transfer reactions) and no direct proton-transfer product ions, $C_nH_{2n+3}^+$, were observed in these experiments.

As shown in Figure 3, the apparent threshold size for H_3O^+ reaction with *n*-alkanes occurs at hexane, just at the point where proton transfer is thermoneutral according to our estimate. The reaction rate constant at 300 K for the hexane reaction is 1% of the collisional rate constant. The reaction efficiency increases steadily with increasing alkane size to 40% for decane where we estimate that proton transfer is 80 kJ mol^{-1} exothermic. Temperature dependences were studied for three alkanes above the threshold size: heptane, octane, and isooctane. In all three cases, the reaction rate constant decreased significantly by 400 K and then showed no additional temperature dependence up to 500 K. The reaction efficiency of H_3O^+ with isooctane does not decrease with temperature as significantly as does the *n*-octane isomer. The decrease is mainly due to the disappearance of the association channel at higher temperatures as described in detail later.

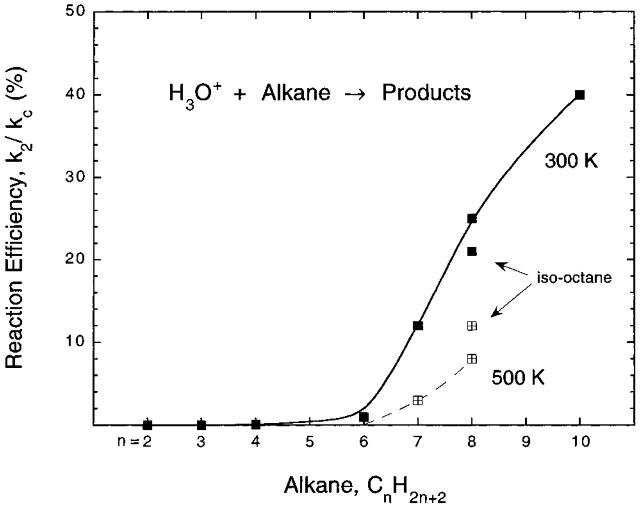

Figure 3. Reaction efficiencies (shown as %) for the reaction of H_3O^+ with *n*-alkanes at 300 K (solid curve) and 500 K (dashed curve). Reaction efficiencies for H_3O^+ with iso-octane at these temperatures are also indicated.

The products of these reactions include numerous alkyl cations and association product ions. For straight-chain C_3-C_{12} alkanes, association is the predominant reaction channel at 300 K, accounting for 50−100% of all product ions. As the polarizability of the alkane increases with size, the ion-induced-dipole interaction is strengthened, increasing the bond strength of the cluster, and the rate constant for this product channel increases. The branching fraction for the association channel in isooctane was 50% less than what was observed in the reaction of octane. Temperature studies of the heptane, octane, and isooctane reactions indicate the association product ions, $C_7H_{16}\cdot H_3O^+$ and $C_8H_{18}\cdot H_3O^+$, are no longer observed at 400 K. The fact that the reaction efficiency for the sum of the nonassociation channels is constant with temperature indicates that association does not compete with reaction.

We believe the overall decrease in the reaction rate constant by 400 K, with no additional temperature dependence up to 500 K, is a result of the association product ions thermally dissociating back into the initial reactants between 300 and 400 K. Although the disappearance of the association products at higher temperatures could also result from a negative temperature dependence of the association rate constant, it seems unlikely in this case given the unusually large temperature dependences that would be required for these products to completely disappear by 400 K, i.e., $> T^{-19}$.

Comparing octane and iso-octane, one finds similar reaction efficiencies at 300 K. However, in the reaction of iso-octane, only 32% of the reactivity is due to association compared with 63% in octane. The reaction efficiency for the nonassociative channels in iso-octane is about 65% larger than for those in octane. Little temperature dependence is observed in the reactivity once the association channels are factored out.

In addition to the association products, H_3O^+ reactions with C_6-C_{12} alkanes also generate a number of smaller alkyl cation products. As shown in Table 1, some of these additional reaction channels are endothermic, and so may not be expected to occur. However, these reactions are expected to involve large entropy changes, and many are therefore expected to be exergonic. The fact that no direct proton-transfer product ions were detected in these experiments could be an indication that the PA's of all the alkanes, up to and including dodecane, are less than that of H_2O, and the proton transfer reactions are therefore endothermic. Alternatively, the presence of the alkyl cations could be an indication that direct proton transfer product ions, once formed, simply dissociate into smaller alkyl fragment ions and neutral alkanes. Smith et al. have previously noted the dissociation of direct proton-transfer product ions in the reaction of H_3O^+ with other organic molecules, especially oxygen-containing species.[16] While proton transfer seems the most likely mechanism for the reaction of H_3O^+ with alkanes, we cannot rule out the possibility that these reactions may occur via other mechanisms such as dissociative hydride or alkide (R^-) transfer.

Aside from the association product ions, the temperature dependence of the product branching fraction is largely due to thermal decomposition of certain product ions. In our previous study of air plasma ions reacting with octane and iso-octane,[2] we observed thermal decomposition of $C_8H_{17}^+$ product ions; $C_8H_{17}^+$ from iso-C_8H_{18} thermally decomposed into *tert*-$C_4H_9^+$ and C_4H_8 at temperatures above 350 K, and $C_8H_{17}^+$ from *n*-C_8H_{18} thermally decomposed into smaller alkyl fragment ions at temperatures above 400 K. Thermal decomposition of $C_8H_{17}^+$ product ions (from reaction of *n*-C_8H_{18}) has also been reported by Matsuoka et al.[17] In the present study, decomposition of $C_8H_{17}^+$ is once again observed. In addition, it appears that $C_7H_{15}^+$ thermally decomposes at temperatures above 400 K, yielding $C_3H_7^+$ and $C_4H_9^+$ fragment ions. $C_6H_{13}^+$ ions may also partially decompose in this temperature range. The evidence is the complete disappearance of the product channel at high temperatures and knowing that the higher mass ions in the homologous series decompose. In contrast, there is no evidence that lower mass alkyl cations, $C_5H_{11}^+$ and smaller, thermally decompose to any extent in the temperature range from 300 to 500 K. Except for this thermal decomposition, there is little temperature dependence in the product branching data, i.e., the branching fractions of the ions are approximately constant with temperature if one adds the decomposition fragment fraction to the parent ion fragment. This could indicate that product ion formation in the reaction of H_3O^+ with alkanes is determined by the position at which the ion attacks the neutral molecule, rather than being governed by rearrangement within the complex.

NO^+ + Alkanes. The reactions of NO^+ with alkanes proceed primarily by hydride transfer:

$$NO^+ + C_nH_{2n+2} \rightarrow C_nH_{2n+1}{}^+ + HNO \qquad (4)$$

The reactions are endothermic for *n*-alkanes smaller than pentane, a fact which correlates well with the very small rate constants found for these molecules. Rate constants obtained at 300 K for the reactions of NO^+ with various C_4-C_{10} alkanes are presented in Figure 4 as a function of alkane size. The present measurements compare favorably with previous results, particularly with the earlier study of Lias et al.[17,18,19] As shown in Figure 4, the NO^+ reaction with *n*-alkanes turns on at hexane; the reaction is 2% efficient for hexane, and the efficiency increases with alkane size up to 60% for decane. Rate constants for the reactions of NO^+ with isoalkanes, which contain tertiary hydrogens, are significantly enhanced compared to the *n*-alkanes. This results from the overall stability of the tertiary carbocation species that is formed in such hydride transfer reactions. There is essentially no temperature dependence of the rate constants for the reactions of NO^+ with alkanes even though they are quite slow. Previously, we reported that the rate constants for octane and isooctane showed no temperature dependence in the range from 300 to 500 K,[2] and an earlier study by Matsuoka et al. also showed no temperature dependence in the rate constants for hexane and octane from 300 to 500 K.[17]

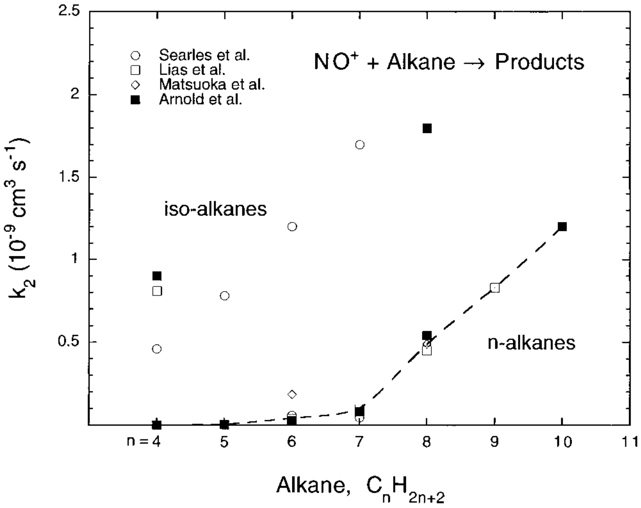

Figure 4. Rate constants for the reaction of NO^+ with *n*-alkanes and isoalkanes. Earlier measurements were taken from refs 17−19.

Our current interest in reexamining this class of ion−molecule reactions lies primarily in determining the product branching fractions for these reactions since our previous study[2] of air plasma ions reacting with octane indicated that the reaction of NO^+ with larger *n*-alkanes does not necessarily proceed exclusively via hydride transfer as indicated in reaction 4. We observed that nearly one-third of the product ions formed from that reaction resulted from channels other than hydride transfer.

The possibility that the additional product ions result from thermal dissociation of larger hydride transfer product ions was explored since experiments at higher temperatures have demonstrated that large alkyl cations such as $C_8H_{17}^+$ do thermally dissociate between 400 and 500 K. However, the product ions which cannot be attributed to hydride transfer at 300 K also do not correlate with the mass of hydride transfer product ion thermal dissociation fragments, which are smaller alkyl cations. Furthermore, in the reaction of NO^+ with C_8H_{18}, product ions of 102, 88, and 74 amu cannot be assigned to thermal dissociation products of $C_8H_{17}^+$ because their branching fractions decrease with increasing temperature between 300 and 400 K before any decrease is observed in the $C_8H_{17}^+$ signal (see Table 2). In our previous report on reactions of atmospheric plasma cations with two isomers of octane,[2] we assigned these product ions as protonated amines of the form $C_mH_{2m+1}NH_3^+$, where $m = 4-6$. This assignment was based on temperature-dependent branching fraction data, which appeared to show loss of 17 amu from these ions with increasing temperature, suggesting the product ions thermally dissociate into a neutral ammonia molecule and an alkyl cation. While such an assignment is consistent with the branching fraction data, it does imply significant rearrangement in the reactions of NO^+ with alkanes. Since that report, we have replaced the operating software on our apparatus and are now capable of detecting ^{18}O and ^{13}C isotopes (from natural abundance) for these reaction products. Using $N^{18}O^+$ as the reactant ion, we found that the product ions at 102, 88, and 74 amu actually contain an oxygen atom, suggesting they are protonated nitrosoalkane cations of the form $C_mH_{2m+1}HNO^+$, where $m = 3-5$. This was confirmed by examining the $^{12}C/^{13}C$ ratio in the product ions.

Protonated nitrosoalkane product ions are also observed in the reaction of NO^+ with other *n*-alkanes, as shown in Table 2. The smallest alkane for which these product ions were observed is pentane; none were observed in the reactions of butane, isobutane, or iso-octane. Overall, the branching fraction of the nonhydride transfer product ions increases with increasing alkane size. For pentane, it represents only 9% of all product ions; for octane, it represents 38% of all product ions formed.

While there is essentially no temperature dependence in the rate constants for the reactions of NO^+ with alkanes, a significant temperature dependence is observed in the product branching fractions for the larger alkanes. The products resulting from hydride transfer, large alkyl cations, thermally dissociate at elevated temperatures. As mentioned earlier, $C_8H_{17}^+$ product ions (from reaction of iso-C_8H_{18}) decompose primarily into *tert*-$C_4H_9^+$ at temperatures above 300 K, $C_8H_{17}^+$ product ions (from reaction of *n*-C_8H_{18}) decompose between 400 and 500 K into $C_5H_{11}^+$ and $C_4H_9^+$ alkyl cations, and $C_7H_{15}^+$ product ions decompose between 400 and 500 K into $C_4H_9^+$. The non-hydride transfer product channels also show significant temperature dependences; the branching fractions for these channels decrease with relatively small increases in temperature. The temperature dependence for these product channels is not straightforward and appears to involve at least two mechanisms: (1) competition between channels that form protonated nitrosoalkane product ions (with corresponding neutral alkenes) and channels that form alkyl product ions and neutral nitrosoalkanes, and (2) possible loss of HNO from the protonated nitrosoalkane product ions.

In previous investigations of the reactions of NO^+ with alkanes, only very brief comments about any product ions other than the hydride transfer product were made. In the reaction of NO^+ with 3-methylhexane, Searles et al.[19] observed $C_4H_9^+$ products in addition to $C_7H_{15}^+$ and attributed this to the fact that the reaction is strongly exothermic and has sufficient energy available for fragmentation processes. Lias et al.[18] noted that small amounts of alkyl ions such as $C_3H_7^+$, $C_4H_9^+$, and $C_5H_{11}^+$ were always present, in addition to the hydride transfer ion, for reactant molecules having five or more carbon atoms. These additional product ions were attributed to fragmentation of the hydride transfer product ion. However, it is possible that these ions are related to the non-hydride transfer product ions observed in the present experiment. If these smaller product ions are stabilized by collisions with the buffer gas, then they may not have been observed previously because earlier measurements were taken at significantly lower pressures than the SIFT measurement, i.e., 0.1−100 mTorr vs 0.4−0.5 Torr.

Trace Gas Analysis of Alkanes. Several chemical ionization instruments have been developed, utilizing H_3O^+, O_2^+, and NO^+ as precursor ions, to detect trace concentrations of various organic species in air and exhaled breath.[6−9] Using such instruments to identify and also quantify components in a complex sample requires prior knowledge of the chemical ionization reaction rate constants and product branching ratios for a large number of organic compounds. Ideally, the chemical ionization reactions proceed at or near the collision rate (for sensitivity) and yield unique product ions (for selectivity). Our laboratory measurements of H_3O^+, O_2^+, and NO^+ reacting with various C_2-C_{12} alkanes significantly expand the kinetic data available on these hydrocarbons. In addition, these results suggest that although H_3O^+, O_2^+, and NO^+ may be suitable chemical ionization agents for many organic compounds, these ions are not suitable for analyzing complex hydrocarbon fuel emissions.

H_3O^+ is not a suitable chemical ionization agent for detecting alkanes because the ion does not react efficiently with alkanes, even at sizes where the proton affinity of the alkane is presumably larger than that of H_2O. In addition, the reaction produces numerous product ions, only one of which is unique for any particular alkane, namely the association product ion. Because H_3O^+ readily proton transfers to alkenes,[20] this ion would probably serve well for chemical ionization detection of alkenes in a simple mixture. However, in a complex sample, containing both saturated and unsaturated hydrocarbons, one could not distinguish alkyl cations resulting from proton transfer to alkenes versus those resulting from fragmentation of alkane proton-transfer product ions.

It has been suggested that O_2^+ is a more appropriate chemical ionization agent for alkanes than H_3O^+ because O_2^+ readily charge transfers to alkanes larger than methane.[8] While these charge-transfer reactions may be very efficient, our laboratory measurements of O_2^+ reacting with two octane isomers[2] and pentane[21] suggest that O_2^+ would not be a suitable chemical ionization agent for alkanes because it does not produce a simple product ion spectrum. We found that O_2^+ reacts readily with both octane isomers and pentane, primarily via dissociative charge transfer. In the case of octane, the branching percentage for the direct charge-transfer product ion, $C_8H_{18}^+$, is only 13% at 300 K. A total of 10 smaller fragment ions, ranging in size from $C_8H_{17}^+$ to $C_3H_5^+$, account for the remaining 87% of the ionic products. In the case of iso-octane, no direct charge-transfer products were observed, although seven dissociative charge-transfer product ions were observed, the most intense products being $C_4H_9^+$ and $C_4H_8^+$. Clearly, it would be very difficult to obtain reliable quantitative information using O_2^+ as a chemical ionization agent for trace gas analysis of alkanes.

Although NO^+ is used for chemical ionization detection of organics such as isoprene, its use for detection of alkanes has not been advocated. We believe that NO^+ would not make a suitable alkane chemical ionization agent for these compounds because the ion does not react rapidly with small *n*-alkanes (the reaction is only 2% efficient for hexane), and the reaction with larger *n*-alkanes yields a number of product ions in addition to the hydride transfer product. The reactions of NO^+ with branched alkanes that contain tertiary hydrogen atoms are very efficient and yield primarily a single hydride transfer product ion. However, it would be difficult to implement a chemical ionization detection scheme based on NO^+ for those molecules alone because of interference which could be expected from the larger straight chain isomers.

Summary

The threshold size for H_3O^+ reaction with *n*-alkanes occurs at hexane, and the reaction rate constants increase steadily with increasing alkane size. Despite the fact that the proton-transfer reaction of H_3O^+ with the larger alkanes is expected to be exothermic, the reaction does not proceed at the collision rate, nor are any direct proton-transfer product ions observed. For straight-chain C_3-C_{12} alkanes, association is the predominant reaction channel at 300 K. Temperature studies suggest the large association product ions thermally dissociate back into the initial reactants between 300 and 400 K. The presence of smaller alkyl product ions could be an indication that direct proton transfer product ions, once formed, simply dissociate into smaller alkyl fragments ions and neutral alkanes.

The threshold size for NO^+ reaction with *n*-alkanes also occurs at hexane, with the reaction efficiency continuing to increase with alkane size. Rate constants for the reactions of NO^+ with isoalkanes, which contain tertiary hydrogens, are significantly enhanced compared to the *n*-alkanes due to the overall stability of the tertiary carbocation species that is formed. There is no temperature dependence of the rate constants for the reactions of NO^+ with alkanes. The reaction of NO^+ with larger alkanes does not proceed exclusively via hydride transfer as previous experiments indicated. Protonated nitrosoalkanes and small alkyl cations are observed in all reactions of *n*-alkanes larger than butane. The branching fraction of the nonhydride transfer product ions increases with increasing alkane size.

With regard to using H_3O^+, NO^+, or O_2^+ as chemical ionization agents for trace gas analysis of mixtures containing a variety of alkanes, the low reaction efficiencies and/or the complex product ion distributions suggest that none of these commonly used ions would be suitable for chemical ionization analysis of alkanes. Furthermore, the use of these ions to quantify unsaturated compounds in complex mixtures containing saturated and unsaturated hydrocarbons will be compromised by interference resulting from reactions with the saturated compounds.

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