Ion–Polar Molecule Collisions. Proton Transfer Reactions of $C_4H_9^+$ Ions with NH_3, CH_3NH_2, $(C_2H_5)_2NH$, and $(CH_3)_3N$

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Abstract: Proton transfer rate constants from $C_4H_9^+$ to NH_3, CH_3NH_2, $(C_2H_5)_2NH$, and $(CH_3)_3N$ have been measured experimentally at thermal energies by ion cyclotron resonance techniques. $C_4H_9^+$ ions are produced from different sources and with various ionizing electron energies. Experimental rate constants are compared with the average dipole orientation (ADO) theory. The reaction efficiencies are less than unity and decrease with increasing ion internal energy. The butyl ions are proposed to be tertiary carbonium ions and an intermediate complex of the collision between $C_4H_9^+$ and the amines is proposed to have the structure $[(CH_3)_3C\text{–}NR_3]^+$.

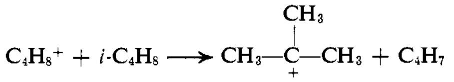
A recent paper from this laboratory[1] has reported the proton transfer reactions from CH_5^+, $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ to NH_3, CH_3NH_2, and $(CH_3)_2NH$. The experimental thermal ion energy rate constants were compared with those predicted by the average dipole orientation (ADO) theory.[1,2] It was observed that in all cases the CH_5^+, $C_2H_5^+$, and $C_3H_7^+$ ions react with essentially unit efficiency while the $C_4H_9^+$ ions react with efficiencies between 0.6 and 0.9. There was no evidence that the size of the ion has an appreciable effect on the magnitude of the reaction rate. The low reaction efficiency for $C_4H_9^+$ proton transfer reactions was ascribed to factors other than ion size. Hellner and Sieck[3] have measured proton transfer rate constants from $C_4H_9^+$ to a number of polar substrates and obtained values quite close to those predicted by the pure polarization theory. They suggested that if proton transfer occurs on every collision, the dipole moment does not significantly increase the collision rate constant, a conclusion that differs from both theoretical predictions[1,2,4] and other experimental results.[1,5,6] In order to investigate the factors that may cause the apparently low reaction efficiency of $C_4H_9^+$ proton transfer reactions and to generate a possible proton transfer mechanism for this particular ion, we have performed a rather intensive study of thermal energy $C_4H_9^+$ proton transfer reactions to NH_3 and three alkyl amines. $C_4H_9^+$ ions are produced from various sources to obtain ions of different internal energies. The variation of the rate constants with internal energy will be discussed. Proton transfer reactions from $C_5H_{11}^+$ to some of the substrates were also studied for comparison.

Experimental Section

The experiments were carried out at 300°K on a homemade icr spectrometer described previously.[7,8] Thermal energy rate constants were determined using the techniques described previously.[2,6] Briefly, a drift cell icr spectrometer was utilized. The intensity of the $C_4H_9^+$ ($C_5H_{11}^+$) ion was monitored as small amounts of substrate were added. The drift times were measured by trapping plate ejection and the pressures measured either directly on an MKS Series 90 capacitance manometer or on a Granville Phillips ion gauge calibrated against the capacitance manometer. Ions were modulated by pulsing the electron beam grid voltage.

$C_4H_9^+$ ions were generated from three sources: (1) neopentane by electron impact; (2) *n*-butyl chloride by electron impact; (3) self-protonation of isobutene.

$$i\text{-}C_4H_8 + e^- \longrightarrow C_4H_8^+ + 2e^- \qquad (1)$$



$$C_4H_8^+ + i\text{-}C_4H_8 \longrightarrow CH_3\text{—}\overset{\overset{\large CH_3}{|}}{\underset{+}{C}}\text{—}CH_3 + C_4H_7 \qquad (2)$$

Various impacting electron energies were used to produce $C_4H_9^+$ from neopentane. $C_5H_{11}^+$ was formed from *n*-pentyl chloride by electron impact. The absolute accuracy of the rate constants is estimated to be within ±15%. The relative values are considerably more accurate, however, within ±5%.

Neopentane, isobutene, ammonia, and the alkyl amines were purchased from Matheson and the alkyl halides were obtained from J. T. Baker Chemical. All chemicals were outgassed before use.

Results

Tables I, II, and III give the measured thermal rate constants of proton transfer reactions of $C_4H_9^+$ from various sources with NH_3, CH_3NH_2, and $(C_2H_5)_2NH$, respectively. The impacting electron energies are indicated. Figures 1 and 2 are plots of reaction rate constants of $C_4H_9^+$ from neopentane with NH_3 and $(CH_3)_3N$, respectively, as a function of the impacting electron energy above the ionization potential of neopentane (10.3 eV). The rate constant obtained when isobutene was used as the source of $C_4H_9^+$ and that

Table I. Proton Transfer Rate Constants from $C_4H_9^+$ to NH_3

Source	Impacting electron energy, eV	$k \times 10^9$ cm³ molecule⁻¹ sec⁻¹ Exptl	ADO	Exptl/ADO
Neopentane	20.0	0.91 (0.90)[a]	1.79	0.51
	10.8	1.16	1.79	0.65
n-C_4H_9Cl	20.0	0.97	1.79	0.54
Isobutene	20.0	1.40	1.79	0.78

[a] From ref 3. Ionization with the 11.6–11.8 eV resonance line of Ar.

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[1] T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, in press.

[2] T. Su and M. T. Bowers, *J. Chem. Phys.*, **58**, 3027 (1973).

[3] L. Hellner and L. W. Sieck, *J. Res. Nat. Bur. Stand., Sect. A*, **75**, 487 (1971).

[4] J. V. Dugan, Jr., and J. L. Magee, *J. Chem. Phys.*, **47**, 3103 (1967).

[5] S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967); A. S. Blair and A. G. Harrison, *ibid.*, **51**, 703 (1973).

[6] T. Su and M. T. Bowers, *J. Amer. Chem. Soc.*, **95**, 1370 (1973).

[7] R. M. O'Malley, K. R. Jennings, M. T. Bowers, and V. G. Anicich, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 99 (1973); V. G. Anicich and M. T. Bowers, *ibid.*, **11**, 555 (1973).

[8] V. G. Anicich, Ph.D. Thesis, University of California at Santa Barbara, 1973.

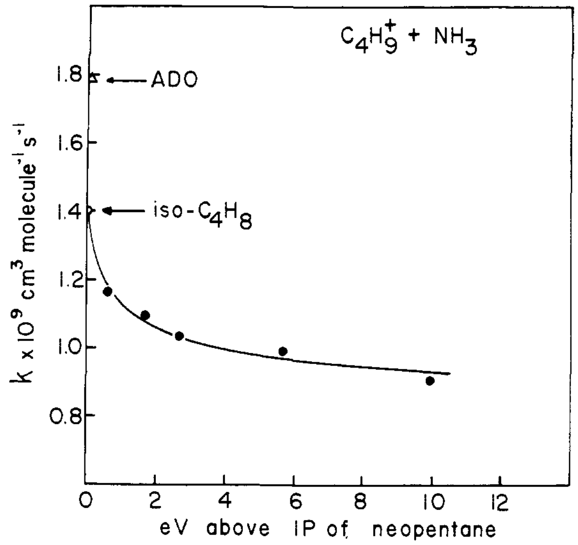

Figure 1. The proton transfer rate constant from $C_4H_9^+$ to NH_3 *vs.* the ionizing electron energy above the ionization potential of neopentane.

Table II. Proton Transfer Rate Constants from $C_4H_9^+$ to CH_3NH_2

Source	Impacting electron energy, eV	$k \times 10^9$ cm^3 molecule^{-1} sec^{-1} Exptl	ADO	Exptl/ ADO
Neopentane	20.0	1.26 (1.30)[a]	1.54	0.82
	10.8	1.31	1.54	0.85
n-C_4H_9Cl	20.0	1.20	1.54	0.78
Isobutene	20.0	1.43	1.54	0.93

[a] From ref 3. Ionization with the 11.6–11.8 eV resonance line of Ar.

Table III. Proton Transfer Rate Constants from $C_4H_9^+$ to $(C_2H_5)_2NH$

Source	Impacting electron energy, eV	$k \times 10^9$ cm^3 molecule^{-1} sec^{-1} Exptl	ADO	Exptl/ ADO
Neopentane	20.0	1.18	1.43	0.83
	10.8	1.23	1.43	0.86
Isobutene	20.0	1.38	1.43	0.97

predicted by ADO theory are included for comparison. Table IV lists the proton transfer rate constants of $C_5H_{11}^+$ (from 20-eV electron impact with *n*-$C_5H_{11}Cl$) with NH_3 and CH_3NH_2.

Table IV. Proton Transfer Rate Constants ($\times 10^9$ cm^3 molecule^{-1} sec^{-1}) of $C_5H_{11}^+$ (from *n*-Pentyl Chloride) to NH_3 and CH_3NH_2

	Exptl	ADO	Exptl/ADO
NH_3	0.65	1.75	0.37
CH_3NH_2	0.91	1.48	0.61

Discussion

Reaction Rates. In Tables I to III, and Figures 1 and 2, it was observed that: (1) all experimental rate constants of $C_4H_9^+$ proton transfer reactions are substantially lower than those predicted by the ADO theory; (2) in all cases in which neopentane or *n*-butyl chloride is used as the source of $C_4H_9^+$ ions, the rate constants are lower than those in which $C_4H_9^+$ is produced from self-protonation of isobutene; (3) for those $C_4H_9^+$ ions formed from electron impact of neopentane, the proton transfer rate constants decrease with increasing impacting electron energy.

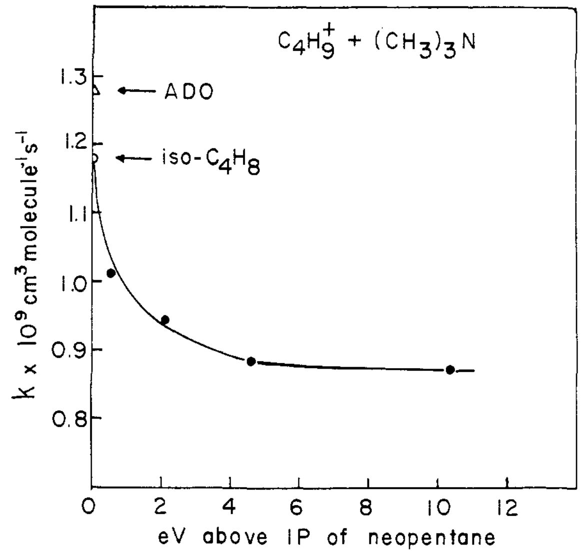

Figure 2. The proton transfer rate constant from $C_4H_9^+$ to $(CH_3)_3N$ *vs.* the ionizing electron energy above ionization potential of neopentane. Hellner and Sieck[3] obtain a value of $1.2 \pm 0.1 \times 10^{-9}$ cm^3/sec using the Ar resonance line (11.6–11.8 eV) ionization of neopentane.

Internal Energy of Ions. It is expected that those ions formed by higher impacting electron energy will have higher internal energy,[9,10] and the $C_4H_9^+$ ions formed by self-protonation of *i*-C_4H_8 will have lower internal energies. The reason is that reaction 2 occurs at thermal kinetic energy, it is only a mildly exothermic reaction (7–14 kcal/mol), the reaction exothermicity and any excitation energy in $C_4H_8^+$ will be partitioned between the two products, and finally because the product $C_4H_9^+$ ions of reaction 2 undergo approximately 10–20 deactivating collisions with *i*-C_4H_8 molecules before colliding with an amine molecule at the pressures at which the experiments were run ($1\text{–}2 \times 10^{-4}$ Torr). Thus, the results of Tables I to III and Figures 1 and 2 indicate that proton transfer rate constants for $C_4H_9^+$ to polar molecules decrease as internal excitation of the ions increases. The 20-eV rate constants are similar for those $C_4H_9^+$ ions produced from either neopentane or butyl chloride. Hence the $C_4H_9^+$ ions are expected to have approximately the same amount of internal excitation from both sources.

Reaction Mechanism. The intermediate complex for ordinary proton transfer reactions such as CH_5^+, $C_2H_5^+$, and $C_3H_7^+$ with NH_3 or methylamines most likely has the proton bound dimer structure I.[11] The

$$R_nC{-}{-}{-}{-}\underset{+}{H}{-}{-}{-}{-}:NR_3$$

I

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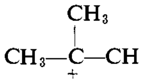
(9) T. O. Tiernan and R. Z. Marcotte, *J. Chem. Phys.*, **53**, 2107 (1970).

(10) T. Su, L. Kevan, and T. O. Tiernan, *J. Chem. Phys.*, **54**, 4871 (1971).

(11) See, for example, M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

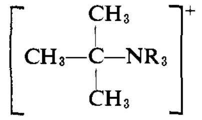
$C_4H_9^+$ ion formed from electron impact with neopentane or self-protonation of isobutene is a tertiary carbonium ion, II, in which there is no hydrogen atom



$$CH_3\overset{\displaystyle CH_3}{\underset{+}{C}}CH_3$$

II

attached to the carbon atom that carries most of the positive charge as there is in CH_5^+, $C_2H_5^+$, or $C_3H_7^+$. The structure of the intermediate collision complex of t-$C_4H_9^+$ with the amines may thus be different from the normal proton bonded dimer. A proposed intermediate has the structure III, in which there is no easily



$$\left[CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-NR_3\right]^+$$

III

accessible site on the nitrogen atom for additional proton attachment. In order for proton transfer to occur, there must be simultaneous breaking of a C–N bond and a C–H bond with the formation of an N–H bond. This concerted mechanism is a rather difficult process compared to the normal proton transfer mechanism *via* the proton bound dimer that requires only a simple bond cleavage. If there is significant internal energy in III, a certain percentage of the complexes will return to reactants by C–N bond scission before the proton transfer occurs. These back reactions result in a low proton transfer efficiency for $C_4H_9^+$. Preliminary quasiequilibrium theory calculations[12] indicate that as the internal excitation of $C_4H_9^+$ increases, the probability of the $C_4H_9NH_3^+$ complex returning to the reactants will increase relative to the probability of proceeding to products. This result is in agreement with the experimental data presented here.

Interestingly, it appears that as the exothermicity of the proton transfer reaction increases, the efficiency increases. This can be seen by comparing the 20-eV $C_4H_9^+$ data for neopentane in the three substrates and the data for $C_5H_{11}^+$ in Table IV.[13] In all cases mixtures of isobutene with the various amines were examined to see if proton transfer from the amine to the hydrocarbon occurred. In no case was a measurable reaction rate observed indicating the proton affinities of the amines are substantially greater than isobutene. The effect of exothermicity on reaction efficiency will be reported in detail at a later date.

When n-C_4H_9Cl was used as a source of $C_4H_9^+$, the resulting proton transfer rate constants were very similar to those obtained with neopentane as the source (Tables I and II). This result suggests that the $C_4H_9^+$ ions generated from n-C_4H_9Cl are tertiary carbonium ions when they react with the amines. The initially formed butyl ions from n-C_4H_9Cl are probably primary carbonium ions originating from a simple C–Cl cleavage. It is expected that n-butyl ion will rearrange to *sec*-butyl ion in a very short time. It has been shown[14] that *sec*-butyl ion rearranges to *tert*-butyl ion within 10^{-9}–10^{-8} sec. The ion residence time in the icr cell is about 10^{-3} sec. Thus essentially all the butyl ions formed from C_4H_9Cl reacting in the icr cell are tertiary, similar to those formed from neopentane.

Similar to butyl ions, $C_5H_{11}^+$ ions formed from n-$C_5H_{11}Cl$ transfer a proton to NH_3 and CH_3NH_2 with reaction efficiencies much lower than unity (Table IV). This result suggests that the n-$C_5H_{11}^+ \rightarrow t$-$C_5H_{11}^+$ isomerization occurs rapidly and that a reaction mechanism similar to that proposed for the t-$C_4H_9^+$ ions is probably occurring. The very low efficiency of reaction 3 indicates the back reaction may be substantial.

$$C_5H_{11}^+ + NH_3 \longrightarrow NH_4^+ + C_5H_{10} \qquad (3)$$

This possibility is being investigated.

Summary

The t-$C_4H_9^+$ ion reacts with polar amine substrates with an efficiency that is strongly dependent on its internal energy. Direct formation of t-$C_4H_9^+$ by electron impact on neopentane and n-butyl chloride results in internally excited ions with reaction efficiencies between 0.5 and 0.9 depending on the electron energy and substrate molecule. $C_4H_9^+$ ions are thus relatively inefficient sources for protons for amine substrates in chemical ionization mass spectrometers that necessarily operate with high energy electron beams. CH_5^+, on the other hand, is very efficient and has the added advantage of offering a higher collision rate constant than $C_4H_9^+$. The low proton transfer efficiency of the $C_4H_9^+$ ion is attributed to the nature of the $C_4H_9^+$–amine collision complex. A C–N bond is presumed to be formed leaving no available orbital on nitrogen to accept the proton. Such may not be the case with other heteroatom substrates (–O, –S, etc.) and this matter is under further investigation.

The suggestion of Hellner and Sieck[3] that $C_4H_9^+$ proton transfer reactions might not exhibit dipole effects with polar substrates results from the decreased efficiency of the $C_4H_9^+$ ion for proton transfer with amines when internal energy is present. This decrease in efficiency brings the observed rate constant fortuitously close to predictions of the Langevin pure polarization theory.[15] In the case of $C_4H_9^+$ reacting with acetone, we have observed that the reaction proceeds in both directions, *i.e.*

$$i\text{-}C_4H_8 + (CH_3)_2\overset{+}{C}OH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_4H_9^+ + (CH_3)_2CO \qquad (4)$$

Our measured rate constant for k_{-4} is in good agreement with the result of Hellner and Sieck and is substantially less than predicted by the ADO theory. A more detailed discussion of reaction 4 will be given in a subsequent paper.[16]

Acknowledgment. The support of the National Science Foundation under Grant No. GP-15628 is gratefully acknowledged.

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[12] W. J. Chesnavich and M. T. Bowers, to be submitted for publication.

[13] Proton transfer from t-$C_4H_9^+$ to NH_3, CH_3NH_2, and $(C_2H_5)_2NH$ is exothermic by 21, 32, and 44 kcal/mol, respectively [J. L. Franklin, *et al.*, *Nat. Stand. Ref. Data Ser.*, *Nat. Bur. Stand.*, **26** (1969); D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972)]. The exothermicity of the $C_5H_{11}^+$ proton transfer reactions is *ca.* 2 kcal/mol lower than the corresponding $C_4H_9^+$ reactions assuming $C_5H_{11}^+$ has a tertiary structure.

[14] S. G. Lias, R. Z. Rebbert, and P. Ausloos, *J. Amer. Chem. Soc.*, **92**, 6430 (1970).

[15] G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

[16] T. Su and M. T. Bowers, to be submitted for publication.