Ion–Polar Molecule Collisions. Proton Transfer Reactions of H_3^+ and CH_5^+ to the Geometric Isomers of Difluoroethylene, Dichloroethylene, and Difluorobenzene

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Abstract: Proton transfer rate constants from CH_5^+, CD_5^+, H_3^+, and D_3^+ to difluoroethylene, dichloroethylene, and difluorobenzene isomers have been measured at thermal ion energies and compared with a classical theory of the ion–dipole interaction. Most experimental rate constants of nonpolar isomers are close to those predicted by the charge-induced dipole theory. Experimental and theoretical results for the polar isomers are also in good quantitative agreement. The effects of a permanent dipole on proton-transfer reactions are much less than predicted by the locked-dipole approximation, and the dipole effect increases with increasing $\mu_D/\alpha^{1/2}$ ratio.

Recent papers from this laboratory[1,2] have reported the charge-transfer reactions of rare gas ions with difluoroethylene, dichloroethylene, and difluorobenzene geometric isomers. It was shown that the effects of a permanent dipole on charge-transfer[1,2] reactions are much smaller than expected by the "locked-dipole" approximation. The average dipole orientations are near $\pi/2$ with respect to the line of collision. A classical theoretical model considering the thermal molecular rotational energy has been developed[2] to estimate the capture cross-sections for ion–dipole reactions. The charge-transfer rate constants previously measured[1,2] were considered to be composed of two components

$$k_T = k_{cap} + k_{ej} \tag{1}$$

k_{cap} corresponds to collisions occurring with impact parameters less than or equal to the capture limit. k_{ej} corresponds to collisions exceeding the capture limit where it is assumed the charge-transfer reaction takes place *via* a nonadiabatic electron jump.[3,4] The theoretical predictions were in excellent agreement with experimental values of k_{cap}. It was assumed that the long-range electron jump reactions show little dependence on the dipole moment.[5] Here, we report a study of the proton-transfer reactions from CH_5^+, CD_5^+, H_3^+, and D_3^+ to the three sets of isomers mentioned above and compare the dipole effects with theoretical predictions. H_3^+ and CH_5^+ are easily accessible sources of protons that can readily be transferred to most gaseous molecules. Such transfers are often highly exothermic due to the low proton affinities of H_2[6,7] and CH_4.[8] These reactions differ from the charge transfer reactions in that a massive particle is transferred rather than an electron and that the transferred particle originates on the impacting ion rather than the neutral molecule. The transfer of a massive particle necessitates a more intimate collision than electron-transfer reactions and thus proton-transfer reactions generally proceed at impact parameters less than or equal to the classical capture limit. This fact will allow direct comparison between experiment and the classical ion–polar molecule theory developed to account for capture collisions[2] and corrections to the experimental data for rate constants exceeding the capture limit need not be made.

Several previous studies have been made on the effects of a dipole moment on proton transfer reactions.[9–13] Gupta, Jones, Harrison, and Myher[11] observed that most low-energy self-protonating reactions of the type

$$RH^+ + RH \longrightarrow RH_2^+ + R \tag{2}$$

proceed with rates slightly larger than the simple polarization theory[14] but considerably less than the locked dipole approximation.[9–11] Hellner and Sieck,[13] on the other hand, observed essentially no dipole effects in reactions of the type

$$t\text{-}C_4H_9^+ + M \longrightarrow MH^+ + C_4H_8 \tag{3}$$

where M was acetone, ammonia, and various methylamines.

The average-dipole-orientation (ADO) theory is summarized as follows.[2] Consider a polar molecule having a permanent dipole moment μ_D being at a distance r from a point positive ion with charge q, making an angle θ with respect to r (see Figure 1). The probability that the dipole is at an orientation θ is

$$P(\theta) \propto \frac{\sin\theta}{\dot{\theta}} \propto \frac{\sin\theta}{[E_{rot} + (q\mu_D/r^2)\cos\theta]^{1/2}} \tag{4}$$

where $\dot{\theta}$ is the angular velocity of the dipole in the plane of the collision, E_{rot} is the thermal rotational energy of the dipolar molecule in the plane of collision, and $\sin\theta$ is a spatial factor accounting for the number of ways

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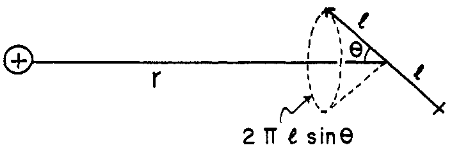

Figure 1. Coordinate system for the interaction between an ion and a linear polar molecule.

the dipole can be oriented with angle θ with respect to the line of centers of the collision. The average value of θ at a certain ion–molecule separation r is then shown in eq 5. In evaluating eq 5 there are two cases to be considered: (1) $E_{\text{rot}} \leq (q\mu_D/r^2)$ and (2) $E_{\text{rot}} \geq q\mu_D/r^2$. In both cases eq 5 can be integrated in terms of elliptic functions.[15] If E_1 and E_2 are the average energies in the plane of collision of all those molecules such that E_{rot} is less than or greater than $q\mu_D/r^2$, respectively, and $\bar{\theta}_1$ and $\bar{\theta}_2$ are the corresponding average values of θ evaluated from eq 5, then

$$\bar{\theta} = \frac{\int \theta \sin\theta \, d\theta/\sqrt{E_{\text{rot}} + (q\mu_D/r^2)\cos\theta}}{\int \sin\theta \, d\theta/\sqrt{E_{\text{rot}} + (q\mu_D/r^2)\cos\theta}} \qquad (5)$$

$$\bar{\theta}(r) = \bar{\theta}_1(r)F_1(r) + \bar{\theta}_2(r)F_2(r) \qquad (6)$$

where $F_1(r)$ and $F_2(r)$ are the fractions of molecules that have E_{rot} less than and greater than $q\mu_D/r^2$, respectively. E_1, E_2, F_1, and F_2 are calculated from the rotational energy distribution function, $P(\epsilon_r)$

$$P(\epsilon_r)\, d\epsilon_r = (1/kT)e^{-\epsilon_r/kT}\, d\epsilon_r \qquad (7)$$

where $P(\epsilon_r)\, d\epsilon_r$ is the probability of finding a molecule with rotational energy between ϵ_r and $\epsilon_r + d\epsilon_r$, k is Boltzmann's constant, and T is the absolute temperature. The effective angle averaged radial potential of the ion–dipole pair is

$$V_{\text{eff}}(r) = \frac{L^2}{2\mu r^2} - \frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2}\cos\bar{\theta}(r) \qquad (8)$$

where L is the translational angular momentum and μ is the reduced mass. The relation between the angle averaged capture cross-section and ion–molecule relative velocity, v, is obtained from $V_{\text{eff}}(r)$ and is given in the following equations[2]

$$\langle\sigma\rangle = \pi r_k^2 + \frac{\pi q^2 \alpha}{r_k^2 \mu v^2} + \frac{2\pi q \mu_D}{\mu v^2}\cos\bar{\theta}_{(r=r_k)} \qquad (9)$$

$$v^2 = \frac{q^2\alpha}{\mu r_k^4} + \frac{q\mu_D}{r_k \mu}\sin\bar{\theta}_{(r=r_k)}\left(\frac{\partial\bar{\theta}}{\partial r}\right)_{r_k} \qquad (10)$$

where r_k is the closest approach which leads to orbiting. By specifying r_k, $\langle\sigma\rangle$ can be plotted as a function of v.

For thermal velocities, the macroscopic rate constant is

$$\bar{k}_{\text{therm}} = \int_0^\infty v\langle\sigma(v)\rangle P(v)\, dv \qquad (11)$$

where $P(v)$ is the Maxwell–Boltzmann distribution of relative velocities. Theoretical thermal rate constants are obtained by integrating eq 11 numerically.

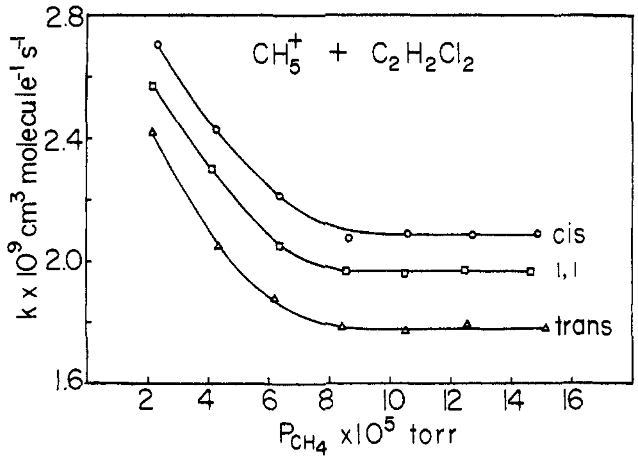

Figure 2. Apparent rate constant, k, for the disappearance of CH_5^+ *via* reaction with the $C_2H_2Cl_2$ isomers as a function of CH_4 pressure.

Experimental Section

The ion cyclotron resonance spectrometer used for the experimental studies is of conventional design and has been discussed in detail elsewhere.[16,17] All experiments were carried out at about 300°K. Reactant ions H_3^+ (or D_3^+) and CH_5^+ (or CD_5^+) were produced by the reactions

$$H_2\cdot^+ + H_2 \longrightarrow H_3^+ + \cdot H \qquad (12)$$

and

$$CH_4\cdot^+ + CH_4 \longrightarrow CH_5^+ + \cdot CH_3 \qquad (13)$$

30-eV electrons were used to form the methane and hydrogen ions. Thermal energy rate constants were measured by observing the decrease of reactant ion intensity at constant methane or hydrogen pressure while increasing the target gas pressure. The detailed experimental techniques were similar to those described previously.[2] It has been observed in the icr and confirmed using resonant ejection double resonance that the reactions between H_3^+, D_3^+, CH_5^+, or CD_5^+ with the substrate molecules used in this work react exclusively by proton transfer or proton-transfer induced dissociation. The apparent rate of disappearance of the reactant ion was measured at various methane or hydrogen backing pressures. Figure 2 shows the apparent rate constants for the reactions $CH_5^+ + C_2H_2Cl_2$ isomers. The following reaction sequence is occurring in the CH_4–$C_2H_2Cl_2$ system

$$CH_4\cdot^+ + CH_4 \longrightarrow CH_5^+ + \cdot CH_3 \qquad (13)$$

$$CH_4\cdot^+ + C_2H_2Cl_2 \longrightarrow \text{products} \qquad (14)$$

$$CH_5^+ + C_2H_2Cl_2 \longrightarrow CH_4 + C_2H_3Cl_2^+ \qquad (15)$$

At low CH_4 pressures, reaction 14 competes with reaction 13. As the $C_2H_2Cl_2$ pressure is increased, the $CH_4\cdot^+$ intensity decreases *via* reaction 14 with a resultant decrease in the amount of CH_5^+ formed *via* reaction 13. Thus it appears that CH_5^+ is reacting with $C_2H_2Cl_2$ at a larger rate than the true rate of reaction 15.

At higher CH_4 pressures reaction 13 overwhelms reaction 14 and the apparent rate constant levels off. The actual proton-transfer (reaction 15) rate constants are taken as the apparent rate constants at the high pressure limit. All rate constants in this work were obtained in a similar way. Each experiment was repeated several times over a period of several months. The measured rate constants were identical within a few per cent. The absolute accuracy of the rate constants is estimated to be ±15%. The relative values between isomeric sets are considerably more accurate, however.

Difluorobenzene, difluoroethylene, and dichloroethylene isomers were purchased from Peninsular ChemResearch Inc., Aldrich Chemical Co., and Chemical Sample Co., respectively, and were thoroughly out-gassed before use. CH_4, CD_4, and H_2 were ob-

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Table I. Proton Transfer Rate Constants from CH_5^+, CD_5^+, H_3^+, and D_3^+ to Difluoroethylene Isomers at 300°K[a]

	Experiment (±15%)			Theory					Trans/induced dipole
				Induced dipole[b]	Present theory		Locked dipole[c]		
	Trans	1,1	Cis		1,1	Cis	1,1	Cis	
CH_5^+	1.02	1.27	1.57	1.31	1.87	2.59	4.84	7.50	0.78
CD_5^+	0.95	1.14	1.35	1.18	1.69	2.34	4.39	6.80	0.80
H_3^+	2.64	3.00	3.60	2.84	4.04	5.60	10.47	16.23	0.93
D_3^+	1.82	2.12	2.70	2.05	2.92	4.05	7.57	11.74	0.92

[a] All rate constants × 10^9 cm^3 molecule^{-1} sec^{-1}. [b] Calculated from charge-induced dipole theory.[14] [c] Calculated from locked-dipole approximation for thermal energies.[11]

Table II. Proton Transfer Rate Constants from CH_5^+, CD_5^+, H_3^+, and D_3^+ to Dichloroethylene Isomers at 300°K[a]

	Experiment (±15%)			Theory					Trans/induced dipole
				Induced dipole[b]	Present theory		Locked dipole[c]		
	Trans	1,1	Cis		1,1	Cis	1,1	Cis	
CH_5^+	1.78	1.97	2.09	1.72	2.13	2.47	5.02	6.37	1.03
CD_5^+	1.54	1.69	1.80	1.51	2.08	2.22	4.48	5.65	1.02
H_3^+	4.00	4.60	5.16	3.90	5.13	5.49	11.25	14.30	1.02
D_3^+	2.86	3.21	3.50	2.78	3.69	3.94	8.06	10.22	1.03

[a] All rate constants × 10^9 cm^3 molecule^{-1} sec^{-1}. [b] Calculated from charge-induced dipole theory.[14] [c] Calculated from locked-dipole approximation for thermal energies.[11]

Table III. Proton Transfer Rate Constants from CH_5^+, CD_5^+, H_3^+, and D_3^+ to Difluorobenzene Isomers at 300°K[a]

	Experiment (±15%)			Theory					Para/induced dipole
				Induced dipole[b]	Present theory		Locked dipole[c]		
	Para	Meta	Ortho		Meta	Ortho	Meta	Ortho	
CH_5^+	1.91	2.12	2.38	1.81	2.28	2.78	5.17	7.64	1.05
CD_5^+	1.50	1.65	1.91	1.62	2.04	2.49	4.62	6.85	0.93
H_3^+	4.90	5.71	6.28	4.10	5.14	6.26	11.66	17.23	1.19
D_3^+	3.37	3.69	4.11	2.93	3.68	4.48	8.34	12.33	1.15

[a] All rate constants × 10^9 cm^3 molecule^{-1} sec^{-1}. [b] Calculated from charge-induced dipole theory.[14] [c] Calculated from locked-dipole approximation for thermal energies.[11]

tained from Matheson, and D_2 from Scientific Gas Products, and were used without further purification.

Results and Discussion

Experimental thermal energy proton transfer rate constants from CH_5^+, CD_5^+, H_3^+, and D_3^+ to difluoroethylene (DFE), dichloroethylene (DCE), and difluorobenzene (DFB) geometric isomers are collected in Tables I–III, respectively, along with the theoretical ADO rate constants calculated from eq 11 and those predicted from the locked dipole approximation.[11] The last column is the ratio of experimental and theoretical rate constants for nonpolar isomers (*trans*-DFE, *trans*-DCE, and *p*-DFB). The polarizability of DFE is obtained from the semiempirical calculation of Beran and Kevan[18] to be 4.20 A^3; those of DCE and DFB are estimated by the LeFevre method[19] to be 7.81 and 8.89 A^3, respectively. Dipole moments are as follows (in Debye units).

DFE: trans 0.00; 1,1 1.38;[20] cis 2.42[20]

DCE: trans 0.00; 1,1 1.34;[20] cis 1.90[20]

DFB: para 0.00; meta 1.58;[20] ortho 2.40[21]

The last column of Tables I–III shows the ratios of trans (or para) to induced dipole rates are close to unity, except for proton transfer from CH_5^+ and CD_5^+ to difluoroethylene, indicating these proton transfer reactions occur at approximately the capture limit. The relatively low trans/induced-dipole ratio for proton transfer from CH_5^+ (or CD_5^+) to DFE (compared with those from H_3^+ or D_3^+) is not well understood. It was felt that a possible equilibrium of the type

$$CH_5^+ + C_2H_2F_2 \rightleftharpoons C_2H_3F_2^+ + CH_4 \qquad (16)$$

might be occurring but resonant ejection double resonance only confirmed the forward reaction.

Since collisions occurring within the capture limit are the only important processes for the proton-transfer reactions of the present study, they provide a suitable set of reactions for direct comparison with the average-dipole-orientation theory.[2] Tables I–III give the overall view of experimental and theoretical rate constants. The experimental rate constants increase with increasing dipole moment but the increase is substantially less than that expected for a locked dipole. With the exception of the difluoroethylene system, the ADO theory predicts rate constants that agree with the experimental values very nearly within experimental error. A more meaningful test of the theory is the comparison of the theoretical and experimental average orientation angles discussed next, however.

The effectiveness of the charge *locking in* the dipole is determined by the relation[1,2]

$$\frac{k_{\text{dipolar}}}{k_{\text{nonpolar}}} = \frac{(2\pi q/\mu^{1/2})(\alpha^{1/2} + c\mu_D(2/\pi kT)^{1/2})}{2\pi q(\alpha/\mu)^{1/2}}$$

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Table IV. Experimental and Theoretical Average Orientation of Dipole for DFE at 300°K

	Experiment				Theory			
	c		$\langle\bar{\theta}\rangle$, deg		c		$\langle\bar{\theta}\rangle$, deg	
	1,1	Cis	1,1	Cis	1,1	Cis	1,1	Cis
CH_5^+	0.091	0.115	84.8	83.4	0.159	0.207	80.9	78.1
CD_5^+	0.075	0.091	85.7	84.8				
H_3^+	0.065	0.084	86.3	85.2				
D_3^+	0.061	0.079	86.5	85.8				

Table V. Experimental and Theoretical Average Orientation of Dipole for DCE at 300°K

	Experiment				Theory			
	c		$\langle\bar{\theta}\rangle$, deg		c		$\langle\bar{\theta}\rangle$, deg	
	1,1	Cis	1,1	Cis	1,1	Cis	1,1	Cis
CH_5^+	0.056	0.067	86.8	86.2	0.124	0.160	82.9	80.8
CD_5^+	0.053	0.062	87.0	86.4				
H_3^+	0.079	0.108	85.5	83.8				
D_3^+	0.065	0.083	86.2	85.2				

Table VI. Experimental and Theoretical Average Orientation of Dipole for DFB at 300°K

	Experiment				Theory			
	c		$\langle\bar{\theta}\rangle$, deg		c		$\langle\bar{\theta}\rangle$, deg	
	Meta	Ortho	Meta	Ortho	Meta	Ortho	Meta	Ortho
CH_5^+	0.049	0.074	87.2	85.8	0.135	0.177	82.2	79.8
CD_5^+	0.047	0.085	87.3	85.1				
H_3^+	0.078	0.096	85.5	84.5				
D_3^+	0.045	0.068	87.4	86.1				

Table VII. Proton Transfer Reactions of *tert*-$C_4H_9^+$ with Some Polar Molecules at 298°K

Polar molecule	μ_D, D	$10^{25}\alpha$, cm^3	10^9k, cm^3/sec			
			Experiment[a]	Langevin	ADO	Locked dipole
$(CH_3)_2CO$	2.88	66.3	1.2	1.09	2.18	6.59
NH_3	1.47	22.6	0.9	0.96	1.74	5.16
CH_3NH_2	1.31	40.1	1.2	1.30	1.50	5.20
$(CH_3)_2NH$	1.03	58.3	1.2	1.20	1.36	3.30
$(CH_3)_3N$	0.61	77.1	1.2	1.25	1.26	2.45

[a] Reference 13.

where c is a parameter with a value between 0 and 1. When $c = 0$ the dipole is totally random and when $c = 1$ the dipole is totally locked. k_{dipolar} stands for the 1,1, cis, ortho, or meta species and k_{nonpolar} stands for the trans or para species. Tables IV–VI compare the experimental and theoretical c values and the corresponding overall average librational angles, $\langle\bar{\theta}\rangle$ ($= \cos^{-1} c$). The experimental values of $(\bar{\theta})$ are near $\pi/2$ and decrease with increasing $\mu_D/\alpha^{1/2}$ ratio. The theory, however, predicts somewhat larger dipole effects than observed experimentally.

There are a number of possible explanations for this discrepancy. The theory does not, for example, account for the finite size of the ion and the polar molecule nor does it account for delocalization of the charge on the polyatomic ionic species. Both of these factors could produce small but significant dipole dependent effects on the experimental rate constants. Inclusion of these effects in the theory and more extensive experimental comparisons are needed to verify these possibilities, however. The important factor, we feel, is that the theory very nearly predicts the dipole effect and the correct magnitude of capture limit collision rate constants between ion and polar molecules. The theory is computationally simple with less than 20 seconds of computer time (IBM 360/75) needed to calculate a thermal energy rate constant. The theory is easy to program with the detailed equations given earlier.[2] It can, then, serve as a diagnostic tool in evaluating reaction efficiencies for ion–polar molecule collisions and can potentially be used for mechanistic arguments. The data of Hellner and Sieck[13] on proton transfer reactions from *tert*-$C_4H_9^+$ to various substrates illustrate this point. They are summarized in Table VII along with the various molecular parameters and theoretical predictions. It is apparent that the data do not show any trend with dipole moment, a result that contrasts with virtually all previously published data and the predictions of theory. Of particular interest are the NH_3 and $(CH_3)_2CO$ data which show deviations much greater than experimental error from the ADO theory capture limit values. On the basis of the results presented here, we cannot conclude that the dipole moment does not affect the *capture* rate constant. It appears, however, that other factors (the great size of the $C_4H_9^+$ ion, possible back reaction from the protonated substrate, etc.) must have considerable influence on the observed *reaction* rate constant. These interesting systems are receiving further study in our laboratories.

Finally, the theory predicts that the dipole effect is independent of the moment of inertia of the polar molecule. From our experimental data, no significant dependence on the moment of inertia was observed. A similar prediction is made by Dugan and Magee[22] in their semiclassical theory of ion trajectories scattered by polar molecules.

Acknowledgment. The support of the National Science Foundation under Grant GP-15628 is gratefully acknowledged.

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