Supplementary Material Available. A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7604.

Ion-Polar Molecule Collisions. The Effect of Molecular Size on Ion-Polar Molecule Rate Constants

Timothy Su and Michael T. Bowers*

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received April 30, 1973*

Abstract: Proton transfer rate constants from CH_5^+ to CH_3Cl, C_2H_5Cl, n-C_3H_7Cl, n-C_4H_9Cl, n-$C_5H_{11}Cl$, i-C_3H_7Cl, i-C_4H_9Cl, t-C_4H_9Cl, and t-$C_5H_{11}Cl$ have been measured experimentally at thermal energies by ion cyclotron resonance techniques and compared with the average dipole orientation (ADO) theory. In all cases the reaction efficiencies are near unity. The dipole moments of all of the compounds are very similar. Thus, the variations in the rate constants are correlated quantitatively with the variations in the polarizability of the polar substrates. No evidence for steric hindrance of proton transfer was found.

Ion-polar molecule collisions have been an area of interest both theoretically[1-3] and experimentally.[2-4] In Langevin's ion-induced dipole theory[5] of ion-nonpolar molecule collisions, it is assumed that both the ion and molecule are point particles. The locked dipole approximation[2,3] and the trajectory calculations[1] of ion-polar molecule collisions are based on the same assumptions. The recently developed average dipole orientation (ADO) theory[6,7] for ion-polar molecule collisions also includes these assumptions. Rate constants predicted by ADO theory are in good agreement with experimental results of some selected ion-dipole systems.[6,8,9] A recent report from this laboratory[7] has also demonstrated that the point particle ADO theory provides a workable model for some selected ion-dipole collisions when the size of the ion is less than a few ångstroms in radius.

In this paper, the ADO theory will be used as a diagnostic tool to investigate the importance of molecular size and structure on the magnitude of capture rate constants. Proton transfer rate constants from CH_5^+ to a number of alkyl chlorides have been measured experimentally (reaction 1) where R represents CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, t-C_4H_9, n-C_5H_{11}, and t-C_5H_{11}. This group of compounds was chosen because they have similar dipole moments but different molecular sizes and configurations.

$$CH_5^+ + R\text{-}Cl \longrightarrow R\text{-}ClH^+ + CH_4 \qquad (1)$$

Results

Experiments were performed at *ca.* 300°K on an icr spectrometer which has been discussed in detail elsewhere.[10,11] Rate constants were measured by the same techniques described previously.[8] The absolute accuracy of experimental rate constants is estimated to be better than ±15%. The relative values are considerably more accurate, *ca.* ±3%. Table I summarizes the thermal energy proton transfer rate constants obtained experimentally and from the ADO theory.[6,7] Rate constants calculated from the Langevin theory and locked dipole approximations are included for comparison. The last column is the ratio of experimental to ADO theoretical rate constants. The polarizabilities, α, and dipole moments, μ_D, of the alkyl chlorides are listed in Table II. (The uncertainty in α is *ca.* ±10% and that of μ_D is *ca.* ±5%. This uncertainty leads to a theoretical uncertainty in the rate constant of *ca.* ±5%.)

Discussion

Theoretical ADO rate constants are in good agreement with experimental values within the theoretical and experimental uncertainty. Both the Langevin zero dipole and the locked dipole models are in marked disagreement with experiment. The experiment/ADO ratios are near unity suggesting that every capture collision leads to reaction. An important observation is that this ratio remains approximately constant despite the substantial change of the physical size and structure of the molecules. Since polarizability is a measure of

---

[1] (a) J. V. Dugan, Jr., and J. L. Magee, *J. Chem. Phys.*, **47**, 3103 (1967); (b) J. V. Dugan, Jr., J. H. Rice, and J. L. Magee, *Chem. Phys. Lett.*, **2**, 219 (1968); (c) J. V. Dugan, Jr., J. H. Rice, and J. L. Magee, *ibid.*, **3**, 323 (1969); (d) J. V. Dugan, Jr., and R. B. Canright, Jr., *ibid.*, **8**, 253 (1971); (e) J. V. Dugan, Jr., and R. W. Palmer, *ibid.*, **13**, 144 (1972); (f) J. V. Dugan, Jr., *ibid.*, **8**, 198 (1971); (g) J. V. Dugan, Jr., and R. B. Canright, Jr., *J. Chem. Phys.*, **56**, 3625 (1972).

[2] T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).

[3] 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**, 1645 (1973).

[4] M. T. Bowers and J. B. Laudenslager, *J. Chem. Phys.*, **56**, 4711 (1972).

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

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

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

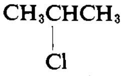
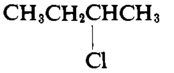
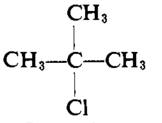
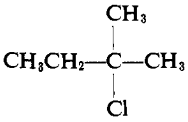
[8] T. Su and M. T. Bowers, *J. Amer. Chem. Soc.*, **95**, 1370 (1973).

[9] M. T. Bowers, T. Su, and V. G. Anicich, *J. Chem. Phys.*, **58**, 5175 (1973).

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

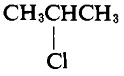
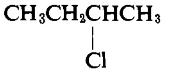
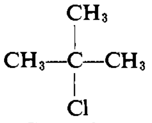
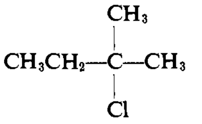
[11] V. G. Anicich, Ph.D. Thesis, University of California at Santa Barbara, 1973.

Table I. Proton Transfer Rate Constants (× 10^9 cm^3 molecule^{-1} sec^{-1}) from CH_5^+ to Alkyl Chlorides at 300°K

	Experiment[a]	ADO[b]	Langevin[c]	Locked[d] dipole	Exptl/ADO
CH_3Cl	2.60	2.41	1.40	6.21	1.08
C_2H_5Cl	3.02	2.66	1.61	6.74	1.13
n-C_3H_7Cl	3.11	2.78	1.80	6.83	1.12
 $CH_3\underset{Cl}{\underset{\vert}{C}}HCH_3$	3.10	2.85	1.80	7.13	1.09
n-C_4H_9Cl	3.20	2.86	1.93	6.90	1.12
 $CH_3CH_2\underset{Cl}{\underset{\vert}{C}}HCH_3$	3.14	2.85	1.93	6.88	1.10
 $CH_3{-}\overset{CH_3}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}{-}CH_3$	3.28	2.90	1.93	7.09	1.13
n-$C_5H_{11}Cl$	3.29	3.03	2.08	7.26	1.09
 $CH_3CH_2{-}\overset{CH_3}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}{-}CH_3$	3.29	3.03	2.08	7.26	1.09

[a] The absolute uncertainty of these numbers is estimated to be within ±15%. The relative values are believed to be accurate to within ±3%, however, and for this reason the results are quoted to two decimal places. [b] Uncertainties in α of *ca.* 10% and μ_D of *ca.* 5% result in an uncertainty in k of *ca.* 5%. The relative values of these numbers is much more accurate, however. [c] Reference 5. $k = 2\pi q(\alpha/\mu)^{1/2}$. [d] $k = (2\pi q/\mu^{1/2})[\alpha^{1/2} + \mu_D(2/\pi kT)^{1/2}]$.

Table II. Polarizabilities and Dipole Moments of Alkyl Chlorides

Substrate	$\alpha \times 10^{25}$ cm^3	μ_D, D
CH_3Cl	45.6[a] (44.5)[c]	1.87[d]
C_2H_5Cl	64.0[a] (62.3)[c]	2.05[d]
n-C_3H_7Cl	82.4[b] (80.3)[c]	2.05[d]
 $CH_3\underset{Cl}{\underset{\vert}{C}}HCH_3$	82.4[b] (80.3)[c]	2.17[d]
n-C_4H_9Cl	98.1[c]	2.05[d]
 $CH_3CH_2\underset{Cl}{\underset{\vert}{C}}HCH_3$	98.1[c]	2.04[d]
 $CH_3{-}\overset{CH_3}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}{-}CH_3$	98.1[c]	2.13[d]
n-$C_5H_{11}Cl$	116.0[c]	2.16[d]
 $CH_3CH_2{-}\overset{CH_3}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}{-}CH_3$	116.0[c]	2.16[e]

[a] H. H. Landolt and R. Bornstein, "Atom and Molecular Physik," Part 3, Springer-Verlag, Berlin, 1950, p 509. [b] E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, **68**, 2926 (1964); E. R. Lippincott, G. Nagorajan, and J. M. Stutman, *ibid.*, **70**, 78 (1966). [c] Estimated by the LeFevre Method: R. J. W. LeFevre, *Advan. Phys. Org. Chem.*, **3**, 1 (1965). [d] R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **10** (1967). [e] A. L. McClellan, "Table of Experimental Dipole Moment," W. H. Freeman, San Francisco, Calif., 1963.

the molecular size and the molecules being studied have similar dipole moments but different polarizabilities, the results in Table I indicate that the effect of molecular size on the rate constants is accounted for quantitatively by the molecular polarizability. In addition, it appears that the rate constant is not sensitive to the physical dimension and geometry of the molecules for this set of reactions. In no case has a steric effect been observed for simple proton transfer reactions of this type.

Calculations of the capture rate constants were also performed using ADO theory modified to include an actual separation of the positive and negative poles of the dipole. This was accomplished by replacing the point charge–point dipole potential with that given in eq 2 and proceeding as before.[6] In (2), r_1 and r_2 are

$$V_D = -q(\mu_D/l)/r_1 + q(\mu_D/l)/r_2 \qquad (2)$$

the distances from the ion to the negative and positive poles of the dipole, respectively, and l is the dipole separation. Only negligible change in the theoretical rate constant is obtained when l is increased from zero to several ångstroms. These calculations suggest the point dipole approximation in the ADO theory is adequate for prediction of capture collision rate constants.

Combining the previous paper on the effects of ion size and the present work, it seems that ion–dipole capture rate constants are relatively insensitive to the physical dimension or configuration of either the ionic or neutral particles. From the limited number of systems experimentally studied,[6–9] it appears that the point particle ADO theory predicts quite accurate capture rate constants for ion–polar molecule reactions where particle radii are less than several ångstroms.

Acknowledgment. This research has been supported by the National Science Foundation under Grant No. GP-15628. We sincerely thank the Foundation for their support. We also thank two referees for their suggestions that substantially improved this manuscript.