Reversible Reactions of Gaseous Ions. VI. The NH_3–CH_4, H_2S–CH_4, and CF_4–CH_4 Systems at Low Temperature

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Abstract: The association of methane with the ions NH_4^+, H_3S^+, and CF_3^+ has been studied. Thermodynamic values have been obtained from the equilibrium constants and their temperature coefficients at temperatures between −80 and −160°. For the formation of $NH_4 \cdot CH_4^+$, $K_{300} = 0.18$, $\Delta G°_{300} = 1.06$ kcal/mol, $\Delta H° = -3.59$ kcal/mol, and $\Delta S° = -15.5$ eu. For the formation of $H_3S \cdot CH_4^+$, $K_{300} = 0.074$, $\Delta G°_{300} = 1.55$ kcal/mol, $\Delta H° = -3.87$ kcal/mol, and $\Delta S° = -18.1$ eu. For the formation of $CF_3 \cdot CH_4^+$, $K_{300} = 0.17$, $\Delta G°_{300} = 1.08$ kcal/mol, $\Delta H° = -4.55$ kcal/mol, and $\Delta S° = -18.8$ eu. Classical electrostatic calculations are made to determine the energy of interaction of methane with the ions NH_4^+, H_3S^+, and CF_3^+. From these calculations we conclude that the experimentally observed enthalpies can be adequately accounted for in terms of ion-induced dipole interactions.

We have found[1,2] that interesting association ions are formed at subambient temperatures in methane and methane–water mixtures. Examples of these ions are $CH_5 \cdot CH_4^+$ (*m/e* 33), $C_2H_5 \cdot CH_4^+$ (*m/e* 45), $CH_5 \cdot (CH_4)_2^+$ (*m/e* 49), $H_3O \cdot CH_4^+$ (*m/e* 35), and $H_3O \cdot (CH_4)_2^+$ (*m/e* 51). Under certain conditions these ions are formed by equilibrium reactions, and the thermodynamic quantities pertaining to the equilibria have been determined. Furthermore, calculations have been made[2] which show that the forces holding these complex ions together are largely or completely classical electrostatic forces.

It is of interest to investigate further the degree of generality of the interactions of various ions with methane and to determine the thermodynamics of any reactions which are discovered. In this paper, we report the results of our investigations of systems NH_3–CH_4, H_2S–CH_4, and CF_4–CH_4.

Experimental Section

The experiments were made using the Esso Chemical Physics mass spectrometer. The apparatus and the experimental technique were identical with those described in our previous papers.[1,2] The materials used were obtained from Matheson, and they were anhydrous ammonia (99.99% minimum), CP hydrogen sulfide (99.6% minimum), tetrafluoromethane (99.7%), and UHP methane (99.97%). Traces of water in the methane were largely removed by

Table I. Mass Spectra in the Methane–Ammonia System[a,b]

m/e	Ion	Relative intensity $I_i/\Sigma I_i$ at t = −68°	−97°	−121°	−143°
17	CH_5^+	0.195	0.215	0.180	0.194
18	NH_4^+	0.368	0.321	0.303	0.118
28	$C_2H_4^+$	0.031	0.026	0.024	0.022
29	$C_2H_5^+$	0.295	0.298	0.275	0.309
31	$C_2H_7^+$	0.007	0.008	0.009	0.022
33	$CH_4 \cdot CH_5^+$	0.004	0.015	0.030	0.073
34	$CH_4 \cdot NH_4^+$		0.003	0.007	0.031
35	$H(NH_3)_2^+$	0.023	0.031	0.056	0.081
41	$C_3H_5^+$	0.031	0.029	0.025	0.023
43	$C_3H_7^+$	0.013	0.011	0.014	0.016
45	$CH_4 \cdot C_2H_5^+$		0.005	0.011	0.058
46	$NH_3 \cdot C_2H_5^+$	0.029	0.030	0.031	0.031
49	$(CH_4)_2 \cdot CH_5^+$				0.006
52	$H(NH_3)_3^+$	0.004	0.005	0.022	0.003
69	$H(NH_3)_4^+$		0.003	0.009	0.003
86	$H(NH_3)_5^+$			0.004	

[a] $P_{CH_4} = 700\ \mu$; $P_{NH_3} = 0.24$–$0.17\ \mu$. [b] Ions due to ^{13}C content omitted from tabulation.

Table II. Mass Spectra in the Methane–Hydrogen Sulfide System[a,b]

m/e	Ion	Relative intensity $I_i/\Sigma I_i$ at t = −81°	−125°	−150°	−159°
17	CH_5^+	0.253	0.209	0.155	0.109
28	$C_2H_4^+$	0.028	0.020	0.018	0.019
29	$C_2H_5^+$	0.294	0.247	0.209	0.222
31	$C_2H_7^+$	0.025	0.024	0.030	0.031
33	$CH_4 \cdot CH_5^+$	0.035	0.124	0.190	0.219
35	H_3S^+	0.257	0.136	0.082	0.058
41	$C_3H_5^+$	0.050	0.041	0.045	0.043
43	$C_3H_7^+$	0.029	0.028	0.032	0.029
45	$CH_4 \cdot C_2H_5^+$	0.002	0.055	0.107	0.118
49	$(CH_4)_2 \cdot CH_5^+$	0.005	0.007	0.018	0.045
51	$CH_4 \cdot H_3S^+$	0.001	0.010	0.028	0.033
63	$H_2S \cdot C_2H_5^+$	0.022	0.058	0.048	0.043
67	$(CH_4)_2 \cdot H_3S^+$			0.002	0.005
69	$H_2S \cdot H_3S^+$		0.041	0.034	0.023

[a] $P_{CH_4} = 900\ \mu$; $P_{H_2S} = 0.17$–$0.10\ \mu$. [b] Ions due to ^{13}C and ^{34}S content omitted from tabulation.

Table III. Mass Spectra in the Methane–Carbon Tetrafluoride System[a,b]

m/e	Ion	Relative intensity $I_i/\Sigma I_i$ at t = −78°	−112°	−149°	−159°
17	CH_5^+	0.335	0.245	0.217	0.202
28	$C_2H_4^+$	0.029	0.023	0.022	0.016
29	$C_2H_5^+$	0.368	0.317	0.281	0.212
31	$C_2H_7^+$	0.032	0.041	0.036	0.035
33	$CH_4 \cdot CH_5^+$	0.014	0.079	0.142	0.138
41	$C_3H_5^+$	0.049	0.058	0.053	0.055
43	$C_3H_7^+$	0.024	0.035	0.034	0.036
45	$CH_4 \cdot C_2H_5^+$	0.011	0,040	0.118	0.174
49	$(CH_4)_2 \cdot CH_5^+$				0.021
69	CF_3^+	0.147	0.135	0.061	0.057
85	$CH_4 \cdot CF_3^+$	0.001	0.014	0.019	0.023
97	$C_2H_4 \cdot CF_3^+$		0.006	0.006	0.007
101	$(CH_4)_2 \cdot CF_3^+$			0.001	0.003
105	$CF_4 \cdot CH_5^+$		0.001	0.001	0.002
157	$CF_4 \cdot CF_3^+$		0.004	0.011	0.014

[a] $P_{CH_4} = 1000\ \mu$; $P_{CF_4} = 41$–$24\ \mu$. [b] Ions due to ^{13}C content omitted from tabulation.

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(1) F. H. Field and D. P. Beggs, *J. Amer. Chem. Soc.*, **93**, 1585 (1971).

(2) S. L. Bennett and F. H. Field, *ibid.*, **94**, 5188 (1972).

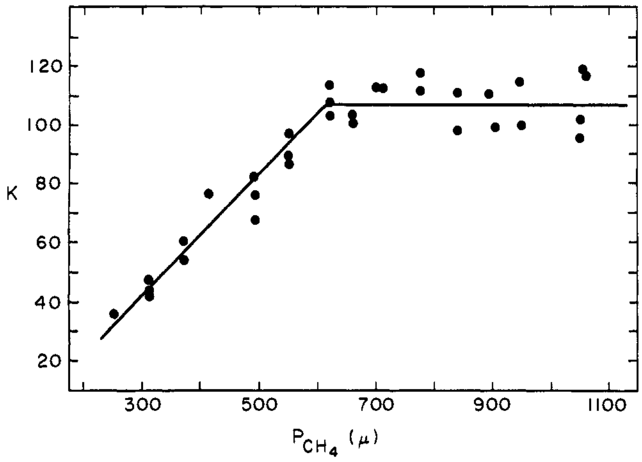

Figure 1. Equilibrium constant *vs.* CH_4 pressure for $NH_4^+ + CH_4 \rightleftharpoons NH_4 \cdot CH_4^+$. $P_{NH_3} = 0.18\ \mu$, $T = -124 \pm 2°$.

passing the methane through a coil submersed in a liquid nitrogen bath.

Results

Tables of the mass spectra obtained at four different temperatures for each of the three systems studied are given in Tables I–III. In these spectra one observes ions formed from the methane alone, ions formed from the inorganic additive (NH_3, H_2S, and CF_4) alone, and ions formed from the methane and the inorganic additive. It is these latter ions upon which we focus our attention. These ions and the reactions by which we think they are formed are shown in eq 1–8. In addition,

$$NH_4^+ + CH_4 \rightleftharpoons \underset{m/e\ 34}{NH_4 \cdot CH_4^+} \tag{1}$$

$$C_2H_5^+ + NH_3 \longrightarrow \underset{m/e\ 46}{C_2H_5 \cdot NH_3^+} \tag{2}$$

$$H_3S^+ + CH_4 \rightleftharpoons \underset{m/e\ 51}{H_3S \cdot CH_4^+} \tag{3}$$

$$H_3S \cdot CH_4^+ + CH_4 \rightleftharpoons \underset{m/e\ 67}{H_3S \cdot (CH_4)_2^+} \tag{4}$$

$$C_2H_5^+ + H_2S \longrightarrow \underset{m/e\ 63}{C_2H_5 \cdot H_2S^+} \tag{5}$$

$$CF_3^+ + CH_4 \rightleftharpoons \underset{m/e\ 85}{CF_3 \cdot CH_4^+} \tag{6}$$

$$CF_3 \cdot CH_4^+ + CH_4 \rightleftharpoons \underset{m/e\ 101}{CF_3 \cdot (CH_4)_2^+} \tag{7}$$

$$CH_5^+ + CF_4 \longrightarrow \underset{m/e\ 105}{CH_5 \cdot CF_4^+} \tag{8}$$

the CH_4–CF_4 system contains an ion with *m/e* 97, which is probably $CF_3 \cdot C_2H_4^+$.

The decision as to whether to represent the reactions included in eq 1–8 as equilibrium reactions or unidirectional reactions is based partly on experimental evidence and partly on analogy. For the NH_3–CH_4 system the equilibrium constant expression for reaction 1, namely, eq 9, exhibits the usual dependence upon methane pressure; namely, it rises initially as the methane pressure is increased but is constant above a certain critical methane pressure. This behavior is illustrated in Figure 1.

$$K = (I_{34}/I_{18})(1/P_{CH_4}) \tag{9}$$

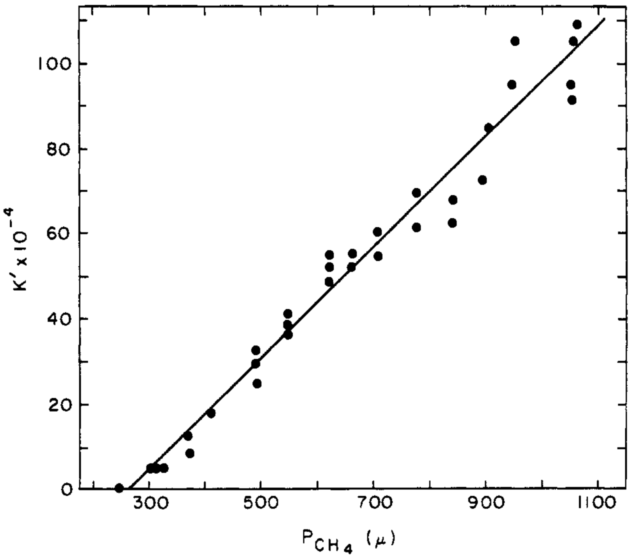

Figure 2. Equilibrium constant *vs.* CH_4 pressure for $CH_5^+ + NH_3 \rightleftharpoons CH_5 \cdot NH_3^+$. $P_{NH_3} = 0.18\ \mu$, $T = -124 \pm 2°$.

An ion with *m/e* 34 could be formed in the methane–ammonia system by the reaction

$$CH_5^+ + NH_3 \rightleftharpoons \underset{m/e\ 34}{CH_5 \cdot NH_3^+} \tag{10}$$

for which the equilibrium constant is

$$K' = (I_{34}/I_{17})(1/P_{NH_3}) \tag{11}$$

If the equilibrium represented in (10) really occurs, the equilibrium constant K' as defined by (11) should exhibit the same kind of dependence upon methane pressure as that depicted in Figure 1. The reason for this is that the methane serves as a third body to stabilize the product formed in (10). Actually, the value of K' rises monotonically as the methane pressure increases over the whole range of pressure available to us with our equipment. This is illustrated in Figure 2. We conclude that reaction 10 does not occur, and this is in accord with our chemical intuition. The proton affinity of ammonia is very much higher than that of methane, and an encounter between CH_5^+ and NH_3 may be expected invariably to result in the transfer of the proton to the NH_3 with the release of a large amount of energy, which would disrupt the complex. A similar situation was encountered in the low-temperature methane–water system.[2]

The value of the equilibrium constant defined by eq 9 is quite dependent upon the pressure of ammonia, undergoing a decrease as the ammonia pressure increases. This is illustrated in Figure 3. The rectangular points on the left-hand ordinate represent the values of the equilibrium constant when the ammonia pressure is reduced to a finite but unmeasurably low value. This general behavior has been observed previously in water systems,[2,3] and as before we attribute the behavior to inability to establish equilibrium in sequential reactions in the time-limited situation which obtains in the ionization chamber of our mass spectrometer. The se-

(3) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, 93, 1567 (1971).

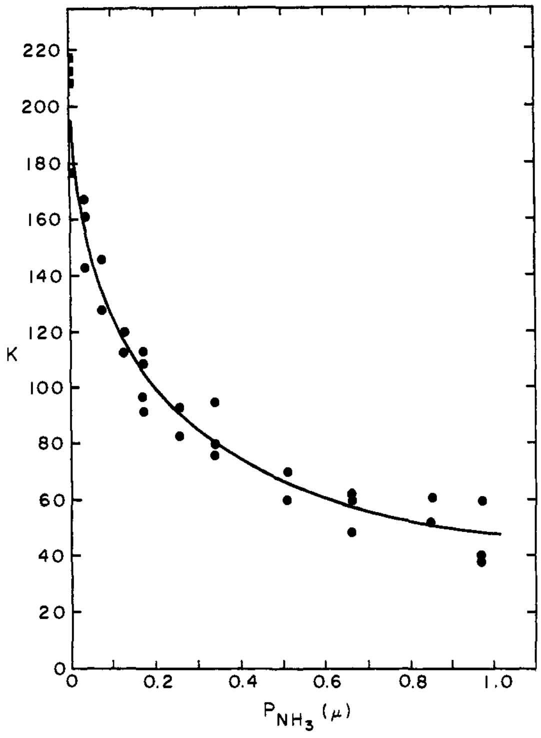

Figure 3. Equilibrium constant *vs.* NH_3 pressure for $NH_4^+ + CH_4 \rightleftharpoons NH_4 \cdot CH_4^+$. $P_{CH_4} = 750\ \mu$, $T = -124 \pm 2°$.

quential reactions which we think are reducing the equilibrium constant (eq 9) are reactions of ammonia with $NH_4 \cdot CH_4^+$, namely

$$NH_4 \cdot CH_4^+ + NH_3 \longrightarrow NH_4 \cdot NH_3^+ + CH_4 \quad (12)$$

To counteract the effect, the measurements of the thermodynamic quantities for the equilibrium were made at the lowest source pressure of NH_3 at which measurements were still possible. These were pressures in the range 0.00016–0.00022 Torr over the temperature range of interest. Even at these low pressures one sees from Figure 3 that the equilibrium constants are slightly below the zero pressure limit, and thus a small experimental error exists.

Reaction 2 is shown as a unidirectional reaction, and this choice was made in analogy with our findings in the methane–water system. There it was shown that the $C_2H_5 \cdot H_2O^+$ ion is formed by a unidirectional reaction, and we would expect no different behavior in the formation of $C_2H_5 \cdot NH_3^+$. We pointed out in the methane–water system[2] that the proton affinity of water is higher than that of ethylene, and thus proton transfer from $C_2H_5^+$ to H_2O should be expected with a concomitant disruption of the complex. Since the proton affinity of ammonia is much higher than that of water, this phenomenon would be more enhanced in the ammonia–methane system. Thus we believe that the $C_2H_5 \cdot NH_3^+$ ion observed in the ammonia–methane spectrum constitutes a highly excited transitory complex.

The experiments described in the ammonia–methane system were also carried out in the hydrogen sulfide–methane system, and the same results were obtained. Thus we believe that $H_3S \cdot CH_4^+$ ion is formed by equilibrium reaction 3. By analogy with reaction 2 we believe that $C_2H_5 \cdot H_2S^+$ is produced by unidirectional reaction 5. The hydrogen sulfide–methane system exhibits an ion with *m/e* 67, which is produced by adding a molecule of methane to $H_3S \cdot CH_4^+$, and we represent this as being an equilibrium reaction in (4). The *m/e* 67 ion is formed in quite small abundance, and detailed experiments were not made on it, but the analogous ion $H_3O \cdot (CH_4)_2^+$ has been found[2] to be formed by an equilibrium reaction.

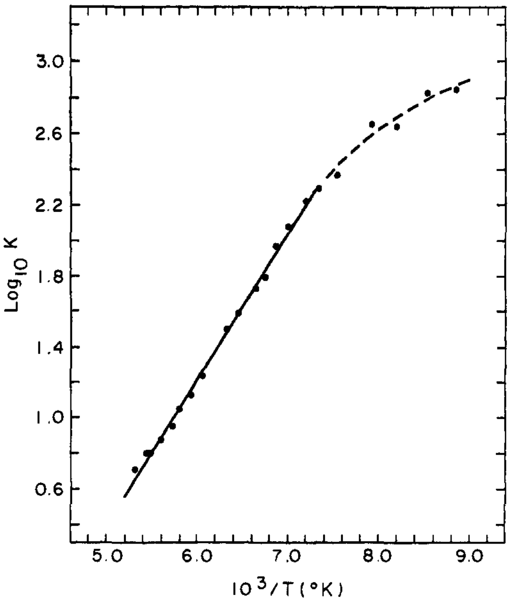

Figure 4. van't Hoff plot for $NH_4^+ + CH_4 \rightleftharpoons NH_4 \cdot CH_4^+$. Standard state = 1 atm, $P_{CH_4} = 800\ \mu$, $P_{NH_3} = 0.22–0.16\ \mu$.

Reactions 6 and 7 in the CF_4–CH_4 system are assumed to be equilibrium reactions by analogy with previous findings in other systems. Because of relatively small intensities, reaction 8 could not be investigated in detail, and we assume that $CH_5 \cdot CF_4^+$ is not formed in an equilibrium reaction. The CF_3^+ ion observed in large abundance in the CF_4–CH_4 spectrum (Table III) is formed by dissociative proton transfer from CH_5^+ to CF_4, and it seems reasonable to guess that the $CH_5 \cdot CF_4^+$ ion written in (8) is just a transient intermediate involved in forming CF_3^+ in (13).

$$CH_5^+ + CF_4 \longrightarrow CF_3^+ + HF + CH_4 \quad (13)$$

Reactions 1, 3, and 6 were investigated at several temperatures. The equilibrium constants were calculated from (9) and analogous expressions for the other systems, and van't Hoff plots were constructed. In all cases the methane pressure was adjusted to a value of 0.8 Torr or above, which is the region wherein the equilibrium constants are independent of methane pressure. The measurements were made with the smallest possible pressure of inorganic additive in order to minimize the diminution of equilibrium constant values as depicted in Figure 3.

The van't Hoff plot obtained for the NH_3–CH_4 system is shown as a typical example in Figure 4. The form of this plot is that which we generally encounter, namely, a linear portion of higher temperatures and a curving portion at low temperatures. As we have discussed in the past,[3,4] the curvature at low temperatures may be ascribed to the onset of nonequilibrium condi-

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(4) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, **93**, 1576 (1971).

Table IV. Experimental Thermodynamic Quantities for Equilibrium Reactions

Equilibrium	K_{300}[a]	$\Delta G°_{300}$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, eu
$NH_4^+ + CH_4 \rightleftharpoons NH_4 \cdot CH_4^+$	0.18 ± 0.06	+1.06 ± 0.21	−3.59 ± 0.11	−15.5 ± 1.1
$H_3S^- + CH_4 \rightleftharpoons H_3S \cdot CH_4^+$	0.074 ± 0.001	+1.55 ± 0.01	−3.87 ± 0.03	−18.1 ± 0.1
$CF_3^+ + CH_4 \rightleftharpoons CF_3 \cdot CH_4^+$	0.17 ± 0.03	+1.08 ± 0.10	−4.55 ± 0.05	−18.8 ± 0.2

[a] Standard state = 1 atm.

tions. The behavior observed in the three systems studied here is in accordance with that predicted from a mathematical analysis of ionic equilibria in mass spectrometers, namely, that the nonlinearity sets in when the product-to-reactant ion ratio is greater than 10–20%.

Duplicate temperature variation determinations were made, and the agreement between them was excellent. Thermodynamic quantities have been obtained from least-squares fits of the linear portions of the van't Hoff plots. The average thermodynamic values obtained are given in Table IV. The limits of error given are the average deviation from the average of the duplicate experiments.

The values of K_{300} for the formation of $NH_4 \cdot CH_4^+$ and $CF_3 \cdot CH_4^+$ are identical. The value for the formation of $H_3S \cdot CH_4^+$ is lower by about a factor of 2. For practical purposes we may consider the values of K_{300}, and equivalently the values of $\Delta G°_{300}$, to be equal for all three systems. The $\Delta H°$ values for the formation of $NH_4 \cdot CH_4^+$ and $CF_3 \cdot CH_4^+$ are different by 1 kcal/mol, and we are inclined to consider this difference to be significant. The $\Delta S°$ value for the formation of $NH_4 \cdot CH_4^+$ is 3 eu less negative than the values obtained for the other two equilibria. The general level of $\Delta S°$ values is about the same as those which we have previously obtained for systems of this sort.

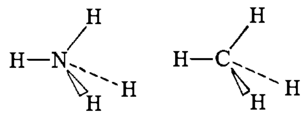
In our previous investigations we obtained[1,2] thermodynamic values for the ions $CH_5 \cdot CH_4^-$ and $H_3O \cdot CH_4^+$. The K_{300} values obtained were 2.1 and 25, respectively. The difference between the thermodynamic values obtained for $CH_5 \cdot CH_4^+$ and $H_3O \cdot CH_4^-$ and those given in Table IV are large enough to be experimentally significant, and they indicate that the $H_3O \cdot CH_4^+$ complex is bound together most tightly, the $CH_5 \cdot CH_4^+$ complex next most tightly, followed by the three complexes studied in this work. This difference in binding is manifested by the fact that the $H_3O \cdot CH_4^+$ ion begins to be formed in our mass spectrometer at an ionization chamber temperature of about +75°, whereas the $NH_4 \cdot CH_4^+$ ion is not formed in detectable amounts until the temperature is lowered to nearly −100°. This difference in binding strength between the methane complexes with H_3O^- and NH_4^+ is interesting and was initially quite puzzling. The $CF_3 \cdot CH_4^+$ ion was investigated to determine if the presence of hydrogen-bonding hydrogen atoms in the reacting ion are necessary for the formation of an association complex. Obviously, they are not.

Electrostatic Calculations

We have described and carried out[2] classical electrostatic ion-induced dipole calculations in the $CH_5 \cdot CH_4^+$ and $H_3O \cdot CH_4^+$ ions. As was mentioned earlier, using these calculations we could account for the general level of the force holding the ions together and for the differences in the enthalpies involved in the formation of the two ions. We have also made such calculations for the $NH_4 \cdot CH_4^+$, $H_3S \cdot CH_4^+$, and $CF_3 \cdot CH_4^+$ ions.

In brief, the procedure involves the calculation of the ion-induced dipole polarization energy using the equations given by Rowell and Stein[5] and the calculation of van der Waals type forces using the Lennard-Jones potential function. The total interaction energies are calculated as a function of distance between the ion and molecule for several different values of the constant σ of the Lennard-Jones potential, and, by comparing minimum values of the interaction energy with the experimentally observed enthalpy, a value of σ appropriate to the system is determined.

The model used for the $NH_4 \cdot CH_4^+$ ion is



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where both NH_4^+ and CH_4 are taken to be tetrahedral with N–H bond distances of 1.03 Å and C–H distances of 1.09 Å. Nitrogen is more electronegative than hydrogen, and significant amounts of polarization of the N–H bonds in NH_4^+ are to be anticipated. Pauling[6] suggests that the formal positive charge in NH_4^+ is equally distributed over the five atoms in the ion. We have made calculations for several different charge distributions in NH_4^+, with values of $\delta_{N^+} = 0.0–1.0$. The values of σ and r (the N–C distance at the minimum of the potential energy curve) obtained for several values of δ_{N^+} are given in Table V. In calculating these values the value of ϵ needed in the Lennard-Jones potential function was obtained from the geometric average of the values of ϵ/k given by Hirschfelder, Curtiss, and Bird[7] for NH_3 and CH_4.

Table V. σ and r Values for $NH_4 \cdot CH_4^+$

δ_{N^+}	σ, Å	r, Å
0.00	3.2_7	3.3_2
0.20	3.3_3	3.2_0
0.50	3.3_7	3.3_0
1.00	3.4_3	3.4_0

One sees from Table V that the results are not very dependent upon the charge distribution assumed in NH_4^+, which is the expected result for such a symmetrical ion. We accept as reasonable the Pauling estimate that the nitrogen atom carries about 20% of the

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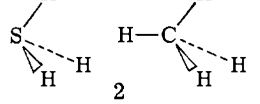
[5] R. L. Rowell and R. S. Stein, *J. Chem. Phys.*, 47, 2985 (1967).

[6] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 102.

[7] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1964.

formal charge, and thus we conclude that for $NH_4 \cdot CH_4^+$, σ = 3.3 Å and r = 3.2 Å. We now examine this value for reasonableness, and we do so by comparing it with the σ values for appropriate neutral compounds. NH_4^+ can be expected to resemble CH_4 in many ways, and thus our σ value for NH_4^+–CH_4 can be compared with the value for CH_4, *i.e.*, σ for the CH_4–CH_4 complex. Hirschfelder, Curtiss, and Bird[7] give the value of 3.81 Å for CH_4, and in our previous calculations for $CH_5 \cdot CH_4^+$ and $H_3O \cdot CH_4^+$ [2] we found that σ values for these ions were roughly 0.4 Å smaller than the σ values for neutral analogs. We see that a similar magnitude contraction occurs in the $NH_4 \cdot CH_4^+$ system, which we take as indicating the reasonableness of our value of σ = 3.3 Å for $NH_4 \cdot CH_4^+$. One can rationalize this ionic contraction in $NH_4 \cdot CH_4^+$ in that, since the hydrogen atoms in NH_4^+ bear a significant fraction of the formal positive charge, their van der Waals radii will be somewhat reduced, which should permit a closer approach of the CH_4 molecule. Also of interest is the comparison of our value of σ = 3.3 Å for $NH_4 \cdot CH_4^+$ with the value found previously[2] of σ = 3.4 Å for $CH_5 \cdot CH_4^+$. Lathan, Hehre, and Pople[8] have suggested a structure for CH_5^+ wherein three of the C–H bonds do not differ very much from tetrahedral bonds and with only slightly greater than normal C–H lengths, and the other two C–H bonds are appreciably longer. The model we used[2] involved the orientation of the tetrahedral-like bonds in CH_5^+ toward the methane, and consequently it is rather to be expected that σ values for $CH_5 \cdot CH_4^+$ and $NH_4 \cdot CH_4^+$ will be about the same.

Turning now to the $H_3S \cdot CH_4^+$ complex, we consider models for the complex analogous to those considered for $H_3O \cdot CH_4^+$.[2] The S–H bond length is taken to be 1.40 Å, which is about 4% larger than the S–H bond distance in H_2S. The electronegativity of sulfur is about equal to that of hydrogen,[9] and thus the electronegativity of charged sulfur will be somewhat greater than that of hydrogen. Consequently, a small amount of polarization of the S–H bonds in H_3S^+ will occur, and we estimate that in this ion the sulfur atom will carry about 0.9 of the formal positive charge. Using this value of δ_{S^+}, we have calculated σ and r values for several models of $H_3S \cdot CH_4^+$. These are analogous to models **2**–**6** of ref 2. The value of ϵ/k = 225 is the geometric average of the values given by Hirschfelder, Curtiss, and Bird[7] for H_2S and CH_4. Because a large preponderance of the formal charge is located on the S atom, the values of σ and r obtained do not vary much from one model to the next, the range being σ = 3.32–3.46 Å and r = 3.20–3.40 Å. As illustrations, the two structures we consider to be most likely and their σ and r values are **2** and **3**.



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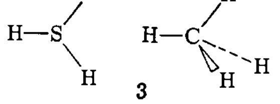
$\sigma = 3.3_9$ Å
$r = 3.3_6$ Å



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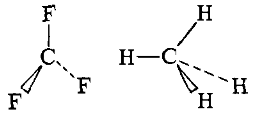
$\sigma = 3.3_7$ Å
$r = 3.2_8$ Å

The most obvious comparison to make of these results is with the results for $H_3O \cdot CH_4^+$. For this ion the most likely values are[2] σ = 2.9 Å and r = 2.8 Å, which means that the σ value in the $H_3S \cdot CH_4^+$ complex is 0.5 Å larger than that in $H_3O \cdot CH_4^+$. The average of the σ values for H_2S and CH_4 is 3.65 Å, while the average of the values for H_2O and CH_4 is 3.15 Å. Here also the difference between the H_2S and H_2O values is 0.5 Å, and the agreement enhances our confidence in the experiments and the calculations for $H_3S \cdot CH_4^+$.

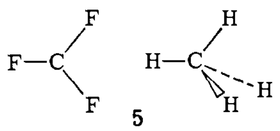
For the calculations on the $CF_3 \cdot CH_4^+$ complex the C–F bond length was taken to be equal to that in CF_4, namely, 1.32 Å.[10a] The CF_3^+ ion was taken to be planar. Pauling[10b] suggests that the C–F bond is polarized to the extent that in CF_4 the carbon atom carries +0.96 of a charge. Then in CF_3^+ it is reasonable to assume that the charge on the central carbon is approximately 1.7, which is less than twice the amount on CF_4 because of the increase in electronegativity of the carbon as the charge on it increases.

The two most likely structures for $CF_3 \cdot CH_4^+$ and values of σ and r calculated for them are **4** and **5**.



4

$\sigma = 3.3_9$ Å
$r = 3.1_4$ Å



5

$\sigma = 3.5_5$ Å
$r = 3.2_0$ Å

The dependence of **4** upon the charge distribution is very mild since σ only varies in the range 3.36–3.39 Å as δ_{C^+} ranges from 1.5 to 1.9. The dependency for **5** is a bit stronger since σ varies between 3.50 and 3.60 over the same range of δ_{C^+}. The value taken for the Lennard-Jones attractive interaction coefficient was ϵ/k = 150°K, which is the geometric average of the values given by Hirschfelder, Curtiss, and Bird[7] for CF_4 and CH_4.

We have no valid way of choosing between structures **4** and **5**, and therefore we take the average of the σ and r values for the two structures as being representative of the $CF_3 \cdot CH_4^+$ complex, namely σ = 3.5 Å at r = 3.2 Å. The value of σ given by Hirschfelder, Curtiss, and Bird[7] for CF_4 is 4.70 Å, and averaging this with the value of 3.81 Å for CH_4 one obtains a value of 4.3 Å for the mixed complex of CF_4–CH_4. Even allowing for some contraction in the ion as has been observed in previous ionic complexes, these two values are not in very good agreement, and we reach the reasonable conclusion that CF_4–CH_4 does not serve as a very good basis of comparison for $CF_3 \cdot CH_4^+$. Perhaps a better calculation can be made for structure **4** as follows. We can approximate the van der Waals radius of the C atom in CF_3^+ by the half-thickness of the aromatic molecule, which Pauling[10c] gives as 1.7 Å. The van der Waals radius of hydrogen is 1.2 Å, and the C–H bond distance in CH_4 is 1.1 Å. Summing these values, we arrive at a figure of 4.0 Å for the C–C distance in $CF_3 \cdot CH_4^+$ without taking into account any ionic shrinkage. If we allow 0.4 Å for this shrinkage, the value for the C–C distance in $CF_3 \cdot CH_4^+$ becomes 3.6 Å, which is in good agreement with the value resulting from our calculation.

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(10) See ref 6: (a) p 314; (b) p 315; (c) p 260.

Table VI. Ionic Collision Radii

Ion	σ, Å	$\sigma - 1.9$, Å	Rel size
CH_5^+	3.4	1.5	1.0
H_3O^+	2.9	1.0	0.7
NH_4^+	3.3	1.4	0.9
H_3S^+	3.4	1.5	1.0
CF_3^+	3.5	1.6	1.1

In this paper and its predecessor,[2] we have made measurements and calculations on five ionic complexes with methane, namely, those involving the ions CH_5^+, H_3O^+, NH_4^+, H_3S^+, and CF_3^+. Our electrostatic considerations adequately account for the initially surprising variations in the enthalpies of reaction for the formation of the several complex ions, and the overall behavior may be considered to be largely understood, namely, as resulting from classical ion-induced dipole interactions.

We can use these results to obtain approximate values for the sizes of the several ions investigated. The σ value for methane is 3.8 Å, and we take half this value as the collision radius in methane. When this collision radius is subtracted from the σ values obtained for the several ionic complexes, we obtain the collision radius for the ion, and these values and their relative magnitudes are tabulated in Table VI.

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Triplet Yield Determinations of Aromatic Compounds

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Abstract: Triplet yields have been determined for pyrazine, monofluorobenzene, *m*-difluorobenzene, and toluene-α,α,α-d_3, using modified forms of the Cundall and biacetyl methods. For pyrazine, determinations were done at several wavelengths, covering both the $n\pi^*$ and $\pi\pi^*$ states. For all cases except that of pyrazine in the $n\pi^*$ state, there is good agreement between the two methods. Both the discrepancy in the one case of pyrazine and the general applicability of these modified procedures are discussed.

Before 1962, when Ishikawa[1,2] developed the photosensitized emission of biacetyl technique, the determination of the efficiency of the intersystem crossing process (ϕ_T) in the vapor phase remained, for the most part, an unanswered question. In 1963, Cundall[3] used the photosensitized isomerization of olefins technique to determine this quantity. To date, there have been numerous papers on the calculation of ϕ_T, particularly for benzene and benzene-type molecules[3-17] based on one or both of these methods.

Despite their obvious popularity, both methods have their attendant disadvantages.[18] Main among these in the Cundall method are interpretation of data and the high pressures of olefin needed to catch all the donor triplet which adversely causes vibrational relaxation. In the biacetyl method there may be a significant quenching of the singlet donor state,[19] thus making interpretation of the results complicated.

Despite the obvious disadvantages of these methods, they are currently the most versatile at the experimenter's disposal.[20] To shed more light on the validity and applicability of these methods, we have investigated several aromatic compounds differing significantly in their structure and substituents.

Experimental Section

Chemicals. *cis*- and *trans*-2-butene were Phillips research grade. The only impurities consisted of 0.048% trans in cis and 0.001% cis in trans, as determined and checked regularly by glc. Biacetyl (Matheson Coleman and Bell) was purified by preparative gas chromatography at 100° using a 20% SE-30 column and doubly distilled *in vacuo*.

m-Difluorobenzene (Eastman Organic Chemicals) was purified as previously described.[21] Monofluorobenzene (Eastman Organic Chemicals) and pyrazine (Aldrich Chemical Co.) were purified as

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