residence time considerations, or result from mass discrimination effects. The calculation of rate constants may not be valid. However, we are unable to think of an error or a combination of errors that is probable enough to warrant suppression of the results. At the same time, prudence dictates that a discussion of their significance be deferred until more experimental results are obtained.

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Effect of Temperature on the Mass Spectra of Benzene at High Pressures

F. H. Field,[1a] Peter Hamlet,[1b,c] and W. F. Libby[1b]

Contribution from the Corporate Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey, and
Department of Chemistry, University of California at Los Angeles, Los Angeles, California. *Received October 26, 1968*

Abstract: The mass spectra of benzene have been obtained as a function of temperature at pressures of 0.5 and 1.0 Torr. The $C_6H_6^+$ and $(C_6H_6)_2^+$ ions are involved in an equilibrium reaction, and the relative amounts of the two ions present in benzene mass spectra depend on temperature. Equilibrium reactions are also found to occur for several minor ions in the benzene spectrum. Thermodynamic quantities for the equilibria are calculated from the temperature coefficients of the equilibrium constants, and it is found that ΔH and ΔS values for the benzene monomer–dimer equilibrium are -15 kcal/mole and -23 cal/(deg mole), respectively.

Two papers have appeared recently on the ion–molecule reactions occurring in benzene gas at elevated pressures.[2] The two works disagree on one important point, namely, the relative amounts of the monomeric benzene ion ($C_6H_6^+$) and dimeric benzene ion ($(C_6H_6)_2^+$) produced. Field, Hamlet, and Libby[2a] found that only a small amount of dimer ion was formed ($I(C_6H_6^+) = 0.57$ and $I((C_6H_6)_2^+) = 0.021$ at $P_{C_6H_6} = 0.34$ Torr), but Wexler and Clow[2b] observed a much higher production of the dimer ion. Their relative amounts seemed to depend upon the electron energy used, but it appears from their Figure 1 that at 400 V and $P_{C_6H_6} = 0.31$ Torr, $I(C_6H_6^+) \cong 0.20$ and $I((C_6H_6)_2^+) \cong 0.30$. The temperature at which their experiments were made was 122°, whereas ours was 236°. This temperature is mistakenly given as 210° in ref 2a. We show in this paper that the relative amounts of the monomeric and dimeric benzene ions are temperature dependent, and the discrepancy in the results obtained by the two groups of workers is the result of the different temperatures used in the two experiments.

Experimental Section

The Esso chemical physics mass spectrometer[3,4] was used in this work. Its application to the determination of the temperature coefficients of mass spectra, equilibrium constants, and rate constants is described in the accompanying paper.[5] The temperature studies of the benzene spectra were made using several different sets of conditions. For two of the runs the benzene pressure was maintained at 0.50 ± 0.01 Torr. In one of these runs the metastable suppressor electrode of the mass spectrometer was not activated, but for the other run it was maintained at a voltage high enough to suppress most of the ions formed by collision-induced dissociation in the near vicinity of the ion exit slit of the ion source. This collision-induced dissociation phenomenon is discussed extensively in ref 5. In the run without the metastable suppressor applied, the intensities of the *m/e* 78 ions were corrected for the contribution from the collision-induced ions by subtracting the intensities of these ions as determined by a visual inspection. To gain some insight into the possible effect of pressure, a run was made at a benzene pressure of 1.0 ± 0.1 Torr. The metastable suppressor electrode was activated. Finally, a run was made on a mixture of approximately 1.0 Torr of CH_4 and 0.55 ± 0.05 Torr of benzene. The metastable suppressor was also activated for this run.

A run in which the pressure of benzene was varied at a source temperature of 92° was made.

The benzene used was zone-refined material obtained from James Hinton Co., Valparaiso, Fla. Toluene was reagent grade from Baker and Adamson, and methane was research grade from Lif-O-Gen.

Results

The temperature studies consisted of determining the spectra of benzene at a number of ionization chamber temperatures between 60 and 200°. The spectra of benzene at a pressure of 0.50 Torr at three temperatures are given in Table I. Of greatest interest is the fact that the relative magnitudes of the intensities

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(1) (a) Esso Research and Engineering Co.; (b) University of California at Los Angeles; (c) supported in part by the Chemical Directorate of the U. S. Air Force Office of Scientific Research, Grant No. AF-AFOSR-67-1255A.

(2) (a) F. H. Field, P. Hamlet, and W. F. Libby, *J. Am. Chem. Soc.*, **89**, 6035 (1967); (b) S. Wexler and R. P. Clow, *ibid.*, **90**, 3940 (1968).

(3) F. H. Field, *ibid.*, **83**, 1523 (1961).

(4) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 2621 (1966).

(5) F. H. Field, *ibid.*, **91**, 2827 (1969).

of $C_6H_6^+$ and $(C_6H_6)_2^+$ undergo a complete inversion between the low- and high-temperature runs. The temperature of the intermediate run (132°) is close to the temperature of the Wexler and Clow experiments (122°),[2b] and the relative magnitudes of the benzene monomer and dimer ions are in acceptable agreement with the values reported by Wexler and Clow ($I(C_6H_6^+) = 0.20$ and $I((C_6H_6)_2^+) \cong 0.30$). Thus we consider the discrepancy between the two works to be resolved.

Table I. Mass Spectra of Benzene at Three Temperatures[a]

m/e	Ion	Relative intensity[b] at 58°	132°	209°
39	$C_3H_3^+$	...	0.024	0.028
63	$C_5H_3^+$	...	0.011	0.012
78	$C_6H_6^+$	0.020	0.30	0.65
79	$C_6H_7^+$	0.055	0.065	0.061
84	$C_4H_4S^+$ (?)	0.009	0.023	...
115	$C_9H_7^+$	...	0.010	0.030
117	$C_6H_6 \cdot C_3H_3^+$	0.031	0.011	...
128	$C_{10}H_8^+$	0.020	0.028	0.026
129	$C_{10}H_9^+$	0.035	0.030	0.028
130	$C_{10}H_{10}^+$	0.012	...	...
141	$C_{11}H_9^+$	0.011	...	...
155	$C_6H_6 \cdot C_6H_5^+$	0.043	0.038	0.037
156	$C_6H_6 \cdot C_6H_6^+$	0.63	0.36	0.020
162	$C_6H_6 \cdot C_4H_4S^+$	0.019	0.001	...
193	$C_6H_6 \cdot C_9H_7^+$ (?)	0.021	0.018	...

[a] $P_{C_6H_6} = 0.50$ Torr. [b] Corrected for C^{13} contributions.

We suggest that the phenomenon can best be rationalized by the postulate that the monomer and dimer ions are in equilibrium, that is

$$C_6H_6^+ + C_6H_6 \rightleftarrows (C_6H_6)_2^+ \tag{1}$$

Several minor ions in the benzene spectrum exhibit changes in intensity as the temperature changes, and we postulate that they also are involved in equilibrium reactions. The most definite relationship is that between the ions m/e 39 and m/e 117, and we write the reaction

$$\underset{m/e\ 39}{C_3H_3^+} + C_6H_6 \rightleftarrows \underset{m/e\ 117}{C_6H_6 \cdot C_3H_3^+} \tag{2}$$

An equilibrium reaction which is suspected but about which some doubt exists is

$$\underset{m/e\ 115}{C_9H_7^+} + C_6H_6 \rightleftarrows \underset{m/e\ 193}{C_6H_6 \cdot C_9H_7^+} \tag{3}$$

Finally, an equilibrium relationship seems to exist between the ions with m/e 84 and m/e 162. It is highly doubtful that these are ions formed from benzene alone, and we suggest that the ion with m/e 84 is the thiophene molecule–ion formed by charge exchange between benzene ions and small amounts of thiophene impurity. The ionization potentials of benzene and thiophene (9.24 and 8.95 V, respectively[6]) would permit this reaction to occur readily. Thus we write

$$C_6H_6^+ + C_4H_4S \longrightarrow C_4H_4S^+ + C_6H_6 \tag{4}$$

$$\underset{m/e\ 84}{C_4H_4S^+} + C_6H_6 \rightleftarrows \underset{m/e\ 162}{C_6H_6 \cdot C_4H_4S^+} \tag{5}$$

It is to be noticed that the intensities of several other minor ions do not vary with temperature. The most notable of these are m/e 79, $C_6H_7^+$, and m/e 155, $C_6H_6 \cdot C_6H_5^+$.

The experiments with added methane ($P_{C_6H_6} = 0.5$ Torr, $P_{CH_4} = 1.0$ Torr) were exploratory in character to investigate the effect of an excess of a substance which would provide an inert third body for the several equilibria. The spectra in the presence of CH_4 were largely unchanged from those in pure benzene, with the notable exception that the $C_6H_7^+$ intensity rose to about 0.32, doubtlessly as a result of the reaction

$$CH_5^+ + C_6H_6^+ \longrightarrow C_6H_7^+ + CH_4 \tag{6}$$

Even with this large intensity of $C_6H_7^+$, no evidence of a reaction to form the protonated dimer of benzene ($C_6H_6 \cdot C_6H_7^+$) was observed. The difference in behavior to the benzene ion and the protonated benzene ion with respect to reaction with benzene molecules is of interest, and equally of interest is lack of reaction producing protonated dimer in benzene as compared with the fact that protonated dimers are produced extensively in benzyl acetate and t-amyl acetate.[5] We can offer no explanation of these differences in behavior, but it is clear that an interesting chemistry is being manifested.

It is of interest to treat the postulated equilibria quantitatively. For the equilibrium

$$A^+ + B \rightleftarrows AB^+ \tag{7}$$

we write the equilibrium constant

$$K_P = \frac{I_{AB^+}}{I_{A^+}} \frac{1}{P_B} \tag{8}$$

where P_B is the pressure of B expressed in atomospheres. The enthalpy and entropy change for the reaction 7 can be obtained from van't Hoff plots of the equilibrium constant, and free energies are in turn obtained from the enthalpies and entropies.

It is assumed in writing (8) that equilibrium is achieved within the ionization chamber and that the ion intensities are accurate measures of ionization chamber concentrations. In previous work in this laboratory,[5] it appeared that equilibrium was obtained in the pure water system and in benzyl acetate and t-amyl acetate ionized by chemical ionization techniques using $i\text{-}C_4H_{10}$ as reactant. In Table II we give equilibrium constants for the $C_6H_6^+$–$(C_6H_6)_2^+$ system as a function of pressure at two source temperatures. The

Table II. Equilibrium Constants at Several Pressures for $C_6H_6^+$–$(C_6H_6)_2^+$ Equilibrium

92°		237°	
$P_{C_6H_6}$, Torr	$10^{-3}K_P$[a]	$P_{C_6H_6}$, Torr	$10^{-3}K_P$[a]
0.039	0.353	0.045	0.059
0.063	1.16	0.118	0.110
0.140	4.31	0.187	0.131
0.187	5.94	0.245	0.124
0.264	7.70	0.302	0.105
0.414	6.98	0.377	0.099
0.610	6.22	0.452	0.101
		0.544	0.088
		0.670	0.062
		0.796	0.065

[a] Standard state = 1 atm.

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(6) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

Table III. Thermodynamic Quantities for Various Equilibria

Equilibrium	Conditions	$\Delta H°$, kcal/mole	$\Delta S°$, cal/(deg mole)	$\Delta G°_{300}$, kcal/mole
$C_6H_6^+$–$(C_6H_6)_2^+$	$P_{C_6H_6} = 0.5$, MSS[a] = off	−15	−23	−8
	$P_{C_6H_6} = 0.5$, MSS = on	−13	−19	−7
	$P_{C_6H_6} = 1.0$, MSS = on	−13	−19	−7
	$P_{C_6H_6} = 0.5$, $P_{CH_4} = 1.0$ MSS = on	−12	−15	−7
$C_3H_3^+$–$C_6H_6 \cdot C_3H_3^+$	All expts combined	−9	−9	−6
$C_4H_4S^+$–$C_6H_6 \cdot C_4H_4S^+$	$P_{C_6H_6} = 0.5$, MSS = off	−13	−23	−7

[a] MSS = metastable suppressor.

values at the higher temperature were calculated from the intensities given in our previous study of benzene.[1] At the lower temperature the equilibrium constant is sensibly constant above approximately 0.2 Torr, although obviously some scatter exists. At the higher temperature the magnitude of the equilibrium constant passes through a maximum at about 0.2 Torr and then exhibits a gentle decline. We can offer no definite explanation for the phenomenon. We believe that at a pressure of 0.5 Torr the equilibrium is well established at the lower temperatures, and the amount of decline in the magnitude of the equilibrium constant occurring at the highest temperatures will not be large enough to cause significant error.

Equilibrium constants have been calculated at the various temperatures for the several equilibria, and thermodynamic quantities have been calculated from the van't Hoff plots of the equilibrium constants. The thermodynamic quantities obtained are given in Table III, and as illustration the van't Hoff plot for the benzene monomer–dimer equilibrium is given in Figure 1. The standard state for the thermodynamic quantities is gas at 1 atm. The points for the van't Hoff plot for the equilibrium given in reaction 3 were so scattered that it seemed inadvisable to calculate thermodynamic quantities.

In the benzene monomer–dimer runs there appears to be a small difference between the results obtained with the metastable suppressor applied and with it not applied. No significant difference is observed between the runs with benzene pressure of 0.5 and 1.0 Torr, and even the addition of 1.0 Torr of CH_4 has little effect on the thermodynamic quantities. We believe that the run with benzene pressure of 0.5 Torr and metastable suppressor off gives the most reliable results.

Recently, Badger and Brocklehurst[7] have used spectroscopic data to obtain a dissociation energy of 14.8 kcal/mole for $(C_6H_6)_2^+$ in the condensed phase. The agreement with our ΔH value of −15 kcal/mole for the formation of the benzene–dimer ion is good. The very close degree of correspondence is not significant, particularly in the light of the possibility of a solvation energy contribution in condensed phase. To provide a comparison, we point out that the reaction enthalpies for some of the gaseous ionic equilibria in the water system are found to range between −15 and −20 kcal/mole.[5] The bond strength for benzene eximer in cyclohexane solution, which also has the benzene rings face to face, is 5.1 kcal/mole,[8] and one would expect the complete removal of one electron from the inter-ring molecular orbitals to increase the binding energy. Thus we are of the opinion that the magnitude of the enthalpy change found in this work is reasonable.

The dimer ion considered by Badger and Brocklehurst[7] was considered to have the sandwich structure. The ion which forms from $C_6H_6^+$ and benzene absorbed on silica gel is of the sandwich type,[9] and furthermore, simple Hückel calculations show that forming the $(C_6H_6)_2^+$ ion in which the rings are bonded at a single point is an endothermic process.[10] In view of all this, we guess that the dimer ion formed in the gas phase has the sandwich structure, although the mass spectrometer provides no direct evidence on this point.

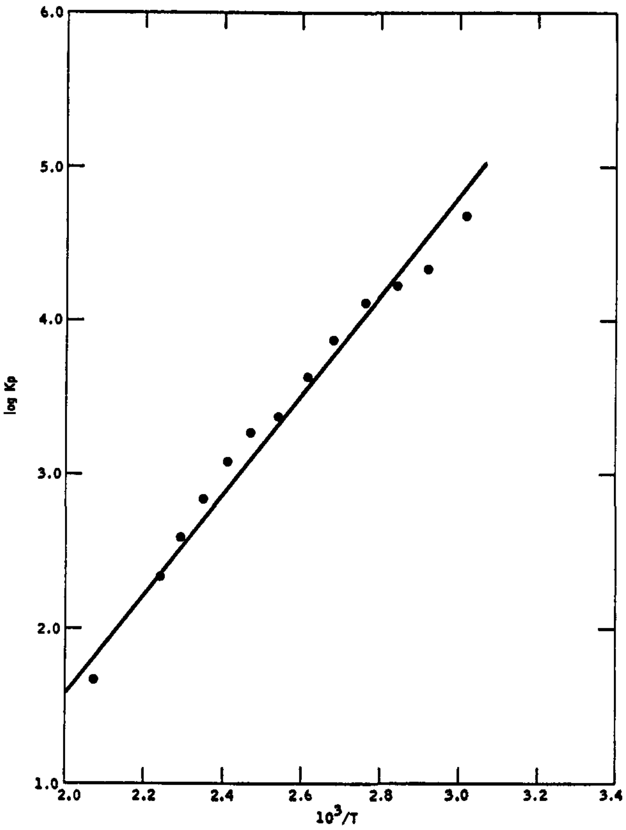

Figure 1. van't Hoff plot for $C_6H_6^+ + C_6H_6 \rightleftarrows (C_6H_6)_2^+$. $P_{C_6H_6}$ = 0.5 Torr, metastable suppressor off.

The entropy change for the formation of the dimer is −23 cal/(deg mole). For purposes of comparison we

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(7) B. Badger and B. Brocklehurst, *Nature*, **219**, 263 (1968).

(8) J. B. Birks, C. L. Braga, and M. D. Lumb, *Proc. Roy. Soc.*, **A283**, 83 (1965).

(9) O. Edland, P. Kinell, A. Lund, and A. Shimizu, *J. Chem. Phys.*, **46**, 3679 (1967).

(10) P. Hamlet, Ph.D. Dissertation, University of California at Los Angeles, 1968; University Microfilms, Ann Arbor, Mich.

cite values of −28 to −33 cal/(deg mole) obtained for several equilibria in the gaseous water system. From dissociation energies and equilibrium constants for the formation of the benzene eximer dimer given by Badger and Brocklehurst,[7] we calculate that the entropy change for the formation of this dimer is −35 cal/(deg mole). All of these values are reasonable in view of the fact that the formation of dimer occurs at the expense of the loss of three translational degrees of freedom, which corresponds to a decrease in entropy of 30–40 cal/(deg mole). Because of experimental uncertainties in these entropy determinations, we are not inclined to attribute great significance to the fact that the entropy change for the formation of the benzene dimer ion is 5–10 cal/(deg mole) less negative than the values for the other two systems.

We give in Table III thermodynamic values for the $C_3H_3^+$–$C_6H_6 \cdot C_3H_3^+$ system, but we wish to point out that the behavior of this system was somewhat anomalous. The van't Hoff plot for the equilibrium constant exhibits a linear decrease in log K with decreasing $1/T$ up to values equivalent to 175°, but above this temperature the change in log K is quite small. We have no explanation for this behavior. The thermodynamic quantities given in Table III are calculated from the linear portion of the plot, but they must be looked upon as having rather uncertain accuracy.

Table III also contains thermodynamic values for the interaction of thiophene with benzene to form the thiophene–benzene ion complex. The intensities of the ions involved in this equilbrium are small (on the order of 2% of the total ionization; see Table I) because of the fact that the thiophene is present as an impurity, but the van't Hoff plot for the equilibrium constant forms an excellent straight line. Therefore, we are of the opinion that the thermodynamic values given in Table III are reasonably reliable. One should note the close similarity of these values with the corresponding values for the benzene monomer–dimer ion equilibrium, but in view of the aromatic character of thiophene and the fact that its ionization potential is not very different from that of benzene, a similarity in the amount of interaction occurring in the two systems is not surprising.

An experiment to investigate the effect of the addition of small amounts of toluene on the benzene system was made. The intensities of the major ions in two benzene–toluene mixtures are given in Table IV. We call attention to the very marked effect that the addition of toluene has to the ion distribution: When the toluene concentration is only 0.1 mole %, ions involving toluene comprise approximately half of the total ionization. From the runs at 2 mole % toluene at two temperatures, it appears that the diminution in the intensities of the toluene–dimer ion and the mixed benzene–toluene association complex ion with increasing temperature is faster than that observed for benzene dimer ion in pure benzene. We have calculated equilibrium constants for the equilibria using the toluene–dimer ion and the benzene–toluene ion, and while we will not quote thermodynamic values based on measurements on only two temperatures, we will say that the equilibrium constants for these ions do change rather rapidly with temperature and that the entropy change for the formation of the two ions from toluene seems to be appreciably more negative than that for the formation of the benzene dimer. Further investigations on the toluene system are in order.

Table IV. Partial Mass Spectra of Benzene–Toluene Mixtures[a]

		Relative intensities[b]		
m/e	Ion	0.1 mole % C_7H_8, 68°	2.1 mole % C_7H_8, 42°	2.1 mole % C_7H_8, 70.5°
78	$C_6H_6^+$	0.032	0.019	0.030
92	$C_7H_8^+$	0.427	0.131	0.529
156	$(C_6H_6)_2^+$	0.175	0.035	0.018
170	$C_6H_6.C_7H_8^+$	0.060	0.199	0.060
184	$(C_7H_8)_2^+$	0.007	0.271	0.057

[a] $P_{C_6H_6}$ = 0.55 Torr. [b] Corrected for C^{13} contributions.