samples containing copper.[8] It is now believed that copper exerts no measurable effect on the activity of MgO itself and that earlier indications to the contrary[8] as well as evidence concerning the poisoning of the H_2–D_2 reaction at 78°K hydrogen adsorption at higher temperatures[8] must be ascribed to artifacts due to the extraordinary sensitivity of the system to traces of water vapor. This can be understood quite readily if the peak concentration of active sites (1 surface site in 10^6) determined by epr is kept in mind. Future work must establish the mode of formation of the active sites and V_I centers as this question was not considered in this investigation.

Besides establishing for the first time a correlation between active sites for a catalytic reaction and epr centers over at least five orders of magnitude of surface concentrations, we have suggested a molecule–ion surface exchange mechanism which is compatible with the low activation energy of the process and relies on protons as surface impurities but not on transition metal ions. An attempt was made to find another related H_2–D_2 equilibration catalyst active at 78°K. The choice was CaO because of its resemblance to MgO and with same rock salt structure. However, this attempt failed indicating that geometric and energetic parameters for the exchange at 78°K are quite demanding. On the other hand, the mechanism of the reaction on Cr_2O_3 appears to be different from that proposed for MgO, since in the case of Cr_2O_3 the activity at 78°K keeps increasing as the sample is pretreated *in vacuo* to higher temperatures; the active site on Cr_2O_3 probably involves a transition metal ion and not a proton.

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Proton Affinities of Benzene, Toluene, and the Xylenes

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Abstract: By operating the ion source of a mass spectrometer at pressures above 0.14 Torr, equilibrium constants have been obtained for the proton transfer reaction of formic acid with benzene, and of both methanethiol and dimethyl ether with toluene and the three xylenes. The resulting free energies when combined with the known proton affinities of the reference compounds (and assuming zero intrinsic entropy of reaction) give the following values for the proton affinities: benzene, 178.0 ± 2.23; toluene, 187.4 ± 1.14; *p*-xylene, 188.0 ± 1.11; *o*-xylene, 188.0 ± 1.09; *m*-xylene, 188.1 ± 1.11, all in kcal/mol. The value for benzene is referred to $\Delta H_f(sec\text{-}C_3H_7^+)$ of 191.7 and all others are referred to $PA[(CH_3)_2O]$ of 187 kcal/mol.

Proton affinity plays an important role in solution chemistry, and values have been obtained by several means for a number of inorganic and aliphatic organic compounds.[1–8] However, the literature gives no information about proton affinities of aromatic compounds except benzene.[3,6,7] We have initiated such an investigation and have started with benzene, toluene, and the xylenes. The results of this first investigation are presented herein.

Experimental Section

The method employed in this study was that of determining the equilibrium constant for a proton transfer reaction of the type

$$\mathrm{MH^+ + R \rightleftarrows RH^+ + M} \tag{1}$$

For this purpose the donor molecule, M, was introduced into the ion source of a quadrupole mass spectrometer at sufficiently high pressure to permit the formation of a large intensity of the protonated donor, MH^+. The donors employed were methanol, formic acid, dimethyl ether and methanethiol. The aromatic, R, was then introduced through a separate heated inlet line into the source at a series of known pressures and the intensities of MH^+ and RH^+ measured. In all cases, the source pressure was sufficiently high to ensure that the ions would undergo a large number of deactivating collisions and thus be as near as possible to the ground vibrational state. In most of the experiments, this was accomplished by using high pressures of the reactants. In one, a high pressure of inert gas (argon) was employed.

All of the gases in these experiments were purchased from Matheson Co. and were used without further purification. Methyl mercaptan and dimethyl ether were research grades of 99.8% purity. Formic acid and toluene were reagent grades of 99.97%.

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Benzene, *o*-xylene, *p*-xylene, and *m*-xylene were chromatoqualities of 99+% purity.

The quadrupole mass spectrometer and experimental procedures have been described.[9] Electrons of 225-eV energy were used to be certain that a sufficient number penetrated well into the ionization chamber to provide an abundance of ions.

Results and Discussion

In the study by Haney and Franklin,[6] two methods involving ion–molecule reactions were employed. In one, the relative translational energy of the products of reaction 2 was determined. It had been shown in a previous study[10] that the translational energy was a nearly constant 20% of the heat of reaction. With these data, the heat of reaction could be determined, and from this the proton affinity was calculated by means of standard thermochemical equations. The proton affinities of methanol, methanethiol, and dimethyl ether were determined in this way.[6] The second method employed a semiqualitative ordering of proton affinities by determining from mixtures the order in which various protonated molecule ions transferred a proton to a second molecule. The proton affinity of benzene had to be determined in this way because benzene does not undergo reaction 2. However, the reaction forming the proton donor, $CH_3OH_2^+$ in this case, was exothermic and so $CH_3OH_2^+$ must have been somewhat excited. The reaction occurred at low pressures and comparatively short times so there was no opportunity for the excess energy to be removed. Thus, Haney and Franklin's[6] value of the proton affinity of benzene might be in error by a few kilocalories per mole.

$$AH^+ + AH \longrightarrow AH_2^+ + A \qquad (2)$$

We wished to determine the proton affinity of benzene, toluene, and the xylenes by reaction 1 but at conditions that would ensure the donor ion's being in the ground state. In order to accomplish this, we kept the source pressure above 140 μ in all experiments. At these conditions an ion would undergo 30–300 collisions before leaving the source.

With each aromatic, donor molecules were chosen which were known or suspected to have a proton affinity close to that of the aromatic of interest. If the proton affinities of the donor and aromatic are within 2–3 kcal/mol, reasonably good values of the equilibrium constant, K, can be obtained. ΔG_R was computed from K using the source temperature of 340°K. We are unable to vary the temperature of our source and thus we cannot determine ΔH_R independently. In all cases we have assumed the intrinsic entropy of reaction 1 to be zero and the heat of reaction was taken to be the free energy corrected for path degeneracy.

Benzene. Haney and Franklin[6] found the proton affinity of benzene to be about 1 kcal/mol greater than that of methanol and about 4 kcal/mol greater than that of formic acid so that either reagent might be suitable for determining PA(C_6H_6) from equilibrium measurements. In a recent study[11] we have redetermined the proton affinities of methanol and formic acid by equilibrium measurements, the resulting values being 179.0 ± 2.15 and 178.0 ± 2.12 kcal/mol, respectively. These values are referred to a heat of formation of isopropyl ion of 191.7 kcal/mol. Thus the absolute values of PA(CH_3OH) and PA(HCOOH) are somewhat lower than those determined approximately by Haney and Franklin.[6] Attempts to determine an equilibrium constant for the reaction

$$CH_3OH_2^+ + C_6H_6 \rightleftarrows C_6H_7^+ + CH_3OH \qquad (3)$$

were only partially successful. In these experiments the methanol pressure was adjusted to give maximum intenity of $CH_3OH_2^+$, at which point only a very small intensity of the $(CH_3OH)_2H^+$ ion was observed. However, when small amounts (up to about 20 μ) of benzene were added, the $(CH_3OH)_2H^+$ ion increased in intensity very rapidly at the expense of $CH_3OH_2^+$. This behavior was quite unexpected and suggests that a very long-lived complex of $CH_3OH_2^+$ and benzene is probably formed and serves as precursor to $(CH_3OH)_2H^+$.

A small intensity of an ion at *m/e* 79 is formed as benzene is added, and after the contribution of the carbon-13 isotope from $C_6H_6^+$ is deduced a very small amount of $C_6H_7^+$ ion remained. At the higher (120–200 μ) pressure of benzene this gave an approximate equilibrium constant of about 0.1 for reaction 3. This corresponds to an approximate free energy of about 1.5 kcal/mol and a proton affinity of benzene of about 177.5 kcal/mol. This result, however, should be taken as, at best, approximate.

Reasonably good values were obtained for the equilibrium constant for reaction 4 as shown in Table I.

$$HCOOH_2^+ + C_6H_6 \rightleftarrows C_6H_7^+ + HCOOH \qquad (4)$$

Table I. Equilibrium Constant for the Reaction

$$HCOOH_2^+ + C_6H_6 \rightleftarrows HCOOH + C_6H_7^+$$

Pressure, μ		Rel abundance		
HCOOH	C_6H_6	$HCOOH_2^+$	$C_6H_7^{+\,a}$	K_{eq}
129	12	78.5	6.26	0.86
129	18	63.3	12.28	1.39
129	68	38.8	18.45	0.90
129	106	20.7	15.50	0.91
129	114	20.8	17.04	0.93
129	138	11.9	16.60	1.30
129	153	9.44	13.27	1.18
170	166	9.31	7.64	0.84
170	175	8.11	9.17	1.10
			Av	1.05 ± 0.17

[a] Corrected for the contribution of the carbon-13 isotope.

Table II. Equilibrium Constant for the Reaction

$$CH_3SH_2^+ + C_4H_4O \rightleftarrows CH_3SH + C_4H_4OH^+$$

Pressure, μ		Rel abundance		
CH_3SH	C_4H_4O	$CH_3SH_2^+$	$C_4H_4OH^{+\,a}$	K_{eq}
195	117	7.45	92.55	20.7
195	145	6.32	93.68	19.8
195	169	5.72	94.28	19.0
195	200	4.91	95.09	18.9
190	237	3.70	96.30	20.8
180	278	2.96	97.04	21.2
180	292	2.94	97.06	20.4
			Av	20.1 ± 0.8

[a] Corrected for the contribution of the carbon-13 isotope.

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Table III. Equilibrium Constant for the Reaction

$$CH_3SH_2^+ + C_6H_5CH_3 \rightleftarrows CH_3SH + C_6H_6CH_3^+$$

Pressure, μ		Rel abundance		
CH_3SH	$C_6H_5CH_3$	$CH_3SH_2^+$	$C_6H_6CH_3^+$ [a]	K_{eq}
216.0	23.0	31.0	35.54	10.8
216.0	30.7	24.1	37.16	10.8
216.0	41.3	18.7	36.01	10.1
216.0	68.0	10.4	26.80	8.18
216.0	82.0	6.72	33.98	13.3
325.4	28.6	45.1	43.08	10.9
361.5	48.8	31.5	41.92	9.86
291.6	122.4	7.7	28.30	8.75
306.0	148.4	7.7	38.38	10.3
354.4	78.6	20.0	39.51	8.91
295.7	75.3	16.2	39.17	9.50
297.4	96.0	10.3	32.22	9.68
190.0	12.0	41.3	23.89	9.15
190.0	18.0	31.5	34.95	11.7
190.0	26.0	28.7	32.58	8.28
			Av	10.01 ± 1.04

[a] Corrected for the contribution of the carbon-13 isotope.

Table IV. Equilibrium Constant for the Reaction

$$(CH_3)_2OH^+ + C_6H_5CH_3 \rightleftarrows C_6H_6CH_3^+ + (CH_3)_2O$$

Pressure, μ		Rel abundance		
CH_3OCH_3	$C_6H_5CH_3$	$CH_3OCH_4^+$	$C_6H_6CH_3^+$ [a]	K_{eq}
134.0	21.0	33.5	5.55	1.06
134.5	29.5	26.7	5.76	0.98
134.5	52.5	12.0	7.87	1.68
134.5	67.5	11.3	8.15	1.44
134.5	99.5	56.0	67.10	1.62
134.5	81.5	8.0	6.67	1.38
134.5	123.5	34.7	27.31	0.86
134.5	148.5	27.0	34.87	1.17
134.5	176.5	16.3	34.30	1.60
134.5	202.7	10.8	23.52	1.44
			Av	1.32 ± 0.26

[a] Corrected for the $[(CH_3)_2O]_2H^+$ ion intensity and for the carbon-13 isotope from the parent ion.

Table V. Equilibrium Constant for the Reaction $(CH_3)_2OH^+ + C_6H_5CH_3 \rightleftarrows C_6H_6CH_3^+ + (CH_3)_2O$

Pressure, μ			Rel abundance		
CH_3OCH_3	Ar	$C_6H_5CH_3$	$CH_3OCH_4^+$	$C_6H_6CH_3^+$ [a]	K_{eq}
55.3	456.7	3.2	38.6	0.253	0.113
55.3	456.7	4.0	38.1	0.278	0.101
55.3	456.7	5.2	37.4	0.428	0.122
55.3	456.7	6.2	36.7	0.428	0.104
55.3	456.7	7.5	36.2	0.56	0.114
55.3	456.7	8.6	34.1	0.67	0.126
55.3	456.7	9.4	36.1	0.71	0.116
55.3	456.7	10.4	35.3	0.652	0.098
55.3	456.7	11.8	34.2	1.12	0.153
55.3	456.7	15.3	33.9	1.25	0.133
55.3	456.7	21.2	31.7	1.51	0.124
				Av	0.119 ± 0.12

[a] Corrected for the $[(CH_3)_2O]_2H^+$ ion intensity and for the carbon-13 isotope from the parent ion.

It should be pointed out that at the formic acid pressures employed the $(HCOOH)_2H^+$ ion was only about 5% as intense as the $HCOOH_2^+$ ion which dominated the spectrum. Further, when benzene was added the intensity of $(HCOOH)_2H^+$ remained essentially constant while that of $HCOOH_2^+$ decayed in accordance with reaction 4. The average value of K_{eq} was 1.05 ± 0.17 which gives $\Delta G = -0.03 \pm 0.11$ kcal/mol. Assuming no entropy change in the reaction, we find $PA(C_6H_6)$ to be 178.03 ± 2.23 kcal/mol. This result, as well as the approximate value mentioned above, shows the proton affinity of benzene to be less than that of methanol and suggests that, in the measurement by Haney and Franklin,[6] some internal energy in the reactant $CH_3OH_2^+$ ion may have helped to bring about reaction.

Toluene. The proton affinities of toluene and the xylenes were expected to be somewhat greater than that of benzene. A few experiments sufficed to show that dimethyl ether and methanethiol would probably be suitable for determining the equilibrium constant for the proton transfer reaction with any of these aromatics. Haney and Franklin[6] have determined the proton affinities of CH_3SH and $(CH_3)_2O$ although, as they stated and as shown in the case of methanol and formic acid, their values involve more uncertainty than would be desired. We accordingly attempted to obtain a more precise value for the relative proton affinities of these two reagents by measuring the equilibrium constant for the reaction

$$CH_3SH_2^+ + (CH_3)_2O \rightleftarrows (CH_3)_2OH^+ + CH_3SH \qquad (5)$$

Unfortunately, several fast ion–molecule reactions occurred in mixtures of methanethiol and methyl ether to the extent that reaction 5 occurred to, at most, a very slight extent. In order to determine the equilibrium constant for (5), therefore, we have employed the expedient of measuring the equilibrium constants for the proton transfer reactions of both methanethiol and methyl ether with furan; thus

$$(CH_3)_2OH^+ + C_4H_4O \rightleftarrows C_4H_4OH^+ + (CH_3)_2O \qquad (6)$$

$$CH_3SH_2^+ + C_4H_4O \rightleftarrows C_4H_4OH^+ + CH_3SH \qquad (7)$$

The equilibrium constant for (6) has previously been determined in this laboratory[12] and was found to be 1.75 ± 0.09 which leads to $PA(C_4H_4O)$ of 187.38 ± 1.04 kcal/mol. As will be seen in Table II, the equilibrium constant for (7) is 20.1 ± 0.8 which leads to a free en-

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(12) S.-L. Chong and J. L. Franklin, unpublished data.

Table VI. Equilibrium Constant for the Reaction

$CH_3SH_2^+ + p\text{-}(CH_3)_2C_6H_4 \rightleftharpoons CH_3SH + p\text{-}(CH_3)_2C_6H_5^+$

Pressure, μ		Rel abundance		
CH_3SH	p-Xylene	$CH_3SH_2^+$	$p\text{-}(CH_3)_2C_6H_5^{+\,a}$	K_{eq}
243.3	40.0	35.0	183.15	31.8
271.8	51.2	12.6	74.93	31.6
275.0	66.0	9.5	85.2	37.4
277.0	76.0	8.0	82.6	37.6
279.0	85.0	6.9	73.76	35.1
282.0	94.0	6.5	73.97	34.1
280.0	122.0	4.2	63.05	34.4
278.0	142.0	3.2	58.0	35.5
277.0	161.0	2.0	46.79	40.3
272.5	172.5	1.8	42.9	37.6
271.0	181.0	1.5	36.15	36.1
			Av	35.7 ± 2.1

[a] Corrected for the contribution of the carbon-13 isotope.

Table VII. Equilibrium Constant for the Reaction

$(CH_3)_2OH^+ + p\text{-}(CH_3)_2C_6H_4 \rightleftharpoons (CH_3)_2O + p\text{-}(CH_3)_2C_6H_5^+$

Pressure, μ		Rel abundance		
CH_3OCH_3	$p\text{-}C_6H_4\text{-}(CH_3)_2$	$CH_3OCH_4^+$	$p\text{-}(CH_3)_2\text{-}C_6H_5^{+\,a}$	K_{eq}
162	94	6.2	3.88	1.08
164	111	4.2	3.40	1.19
163	130	3.5	3.53	1.26
159	152	2.2	3.55	1.69
209	152	1.7	1.88	1.52
118	152	2.0	3.74	1.45
90	167	1.3	4.42	1.84
82	186	1.0	3.95	1.74
294	46	15.4	3.35	1.39
277	111	8.4	3.85	1.14
273	130	6.4	3.90	1.28
267	152	5.3	3.38	1.12
131	152	6.2	11.05	1.54
138	111	9.5	11.6	1.52
			Av	1.41 ± 0.20

[a] Corrected for the contribution of the carbon-13 isotope.

ergy of reaction of −2.05 ± 0.03 kcal/mol. When correction is made for path degeneracy, the resulting heat of reaction 7 is −1.58 ± 0.03 kcal/mol and the proton affinity of methanethiol is 185.8 ± 1.07 kcal/mol, in fair agreement with Haney and Franklin's[6] value. The proton affinities of both methanethiol and furan are arbitrarily referred to that of methyl ether as 187.0 ± 1 kcal/mol as given by Haney and Franklin.[6] It is our intention ultimately to place this value on a firmer absolute basis.

In the toluene study, both reagents CH_3OCH_3 and CH_3SH were employed. The results obtained with methanethiol are given in Table III and show the equilibrium constant to be 10.01 ± 1.04 which leads to a free energy of reaction of −1.57 ± 0.07 kcal/mol.

An attempt was also made to determine the equilibrium constant when using protonated dimethyl ether as the protonating agent. Unfortunately, at the pressures necessary to obtain a high intensity of the $(CH_3)_2OH^+$ ion, some $[(CH_3)_2O]_2H^+$ ion was always present. This ion has the same mass as does the protonated toluene ion and thus makes an accurate determination of the intensity of $C_6H_6CH_3^+$ impossible. We have attempted to correct for the contribution of $[(CH_3)_2O]_2H^+$ to the m/e 93 ion intensity by assuming it to be constant with results given in Table IV. In a further effort to circumvent the problem, we employed considerably smaller

Table VIII. Equilibrium Constant for the Reaction

$CH_3SH_2^+ + o\text{-}(CH_3)_2C_6H_4 \rightleftharpoons CH_3SH + o\text{-}(CH_3)_2C_6H_5^+$

Pressure, μ		Rel abundance		
CH_3SH	o-Xylene	$CH_3SH_2^+$	$o\text{-}(CH_3)_2\text{-}C_6H_5^{+\,a}$	K_{eq}
215.5	40.5	10	74.51	39.6
226.8	51.7	9.0	86.81	42.4
230.0	65.0	8.0	76.65	33.9
240.9	79.1	7.0	78.99	34.4
247.3	85.0	8.0	93.68	34.1
248.3	91.7	7.2	97.67	36.8
249.0	104.0	5.7	88.87	37.4
247.0	119.0	5.0	79.69	33.1
240.0	134.0	3.3	75.19	40.9
218.0	155.4	2.0	63.83	44.7
217.7	178.6	1.5	50.8	41.2
			Av	38.0 ± 3.3

[a] Corrected for the contribution of the carbon-13 isotope.

Table IX. Equilibrium Constant for the Reaction

$(CH_3)_2OH^+ + o\text{-}(CH_3)_2C_6H_4 \rightleftharpoons (CH_3)_2O + o\text{-}(CH_3)_2C_6H_5^+$

Pressure, μ		Rel abundance		
CH_3OCH_3	o-Xylene	$CH_3OCH_4^+$	$o\text{-}(CH_3)_2\text{-}C_6H_5^{+\,a}$	K_{eq}
153.4	16.6	37	6.21	1.55
157.6	23.4	37.8	7.85	1.40
158	30	37.3	14.29	2.02
156	49	13	6.31	1.54
157.4	58	12	6.46	1.46
157.1	68.4	11	7.09	1.48
156.7	78.7	9.8	8.23	1.67
156.7	90.6	7.2	7.23	1.74
157	102	7.0	7.14	1.57
157.5	112.5	6.1	6.57	1.51
243.5	112.5	5.7	3.62	1.39
259.7	12.3	50.6	3.64	1.52
257.6	23.4	43.3	6.3	1.60
255.7	30	49	9.14	1.59
254.5	39.5	46.2	10.98	1.53
252	58	42	13.05	1.35
251.6	68.4	33.5	14.1	1.55
251.6	78.7	31.3	14.74	1.50
251.1	90.6	26.7	16.7	1.73
250	102	24.4	16.4	1.65
			Av	1.58 ± 0.11

[a] Corrected for the contribution of the carbon-13 isotope.

Table X. Equilibrium Constant for the Reaction

$CH_3SH_2^+ + m\text{-}(CH_3)_2C_6H_4 \rightleftharpoons CH_3SH + m\text{-}(CH_3)_2C_6H_5^+$

Pressure, μ		Rel abundance		
CH_3SH	m-Xylene	$CH_3SH_2^+$	$m\text{-}(CH_3)_2\text{-}C_6H_5^{+\,a}$	K_{eq}
208.4	53.6	8.5	78.08	35.8
203.8	71.2	3.4	52.02	43.3
201.1	93.3	6.0	107.29	38.6
199.0	101	4.3	114.22	52.4
197.7	108.9	4.1	103.02	45.6
195.2	116.8	3.2	93.52	48.9
196.0	133	2.5	71.58	42.2
			Av	43.8 ± 4.4

[a] Corrected for the contribution of the carbon-13 isotope.

Table XI. Equilibrium Constant for the Reaction

$$(CH_3)_2OH^+ + m\text{-}(CH_3)_2C_6H_4 \rightleftarrows (CH_3)_2O + m\text{-}(CH_3)_2C_6H_5^+$$

Pressure, μ		Rel abundance		
CH_3OCH_3	*m*-Xylene	$CH_3OCH_4^+$	*m*-$(CH_3)_2$-$C_6H_5^{+\,a}$	K_{eq}
188.3	83.7	21	13.76	1.47
180.8	112.4	20	17.56	1.41
181	128.2	13.4	18.88	1.99
179.9	44.1	79	35	1.81
183.5	97.1	13.4	12.4	1.75
298.5	70.5	36.6	10.29	1.19
392.5	16.9	54.5	3.72	1.59
396.2	24.2	44.3	4.0	1.48
396.9	44.1	30.5	5.67	1.68
398	56	23	6.24	1.93
390.9	70.5	17.7	5.32	1.67
392.3	83.7	16.2	5.10	1.48
417.1	24.2	47.7	4.72	1.70
341	34.2	71.5	8.82	1.23
383.5	10.7	150.9	6.64	1.58
398	34.2	33.9	5.74	1.97
			Av	1.60 ± 0.19

[a] Corrected for the contribution of the carbon-13 isotope.

Table XII. Proton Affinities

Compound	K_{eq}	ΔH, kcal/mol		Proton affinity of aromatic, kcal/mol
Benzene				
HCOOH	1.05 ± 0.17	−0.03 ± 0.11		178.03 ± 2.23
Toluene				
CH_3SH	10.01 ± 1.04	−1.57 ± 0.07		187.37 ± 1.14
p-Xylene				
CH_3SH	35.7 ± 2.1	−2.44 ± 0.04		188.24 ± 1.11
CH_3OCH_3	1.41 ± 0.20	−0.71 ± 0.1		187.71 ± 1.1
			Av	187.98 ± 1.11
o-Xylene				
CH_3SH	38.0 ± 3.3	−2.48 ± 0.06		188.28 ± 1.13
CH_3OCH_3	1.58 ± 0.11	−0.78 ± 0.05		187.78 ± 1.05
			Av	188.03 ± 1.09
m-Xylene				
CH_3SH	43.8 ± 4.4	−2.58 ± 0.07		188.38 ± 1.14
CH_3OCH_3	1.60 ± 0.19	−0.79 ± 0.08		187.79 ± 1.08
			Av	188.09 ± 1.11

pressures of the reactants along with some 450 μ of argon. The results are given in Table V.

The proton affinities given in Table XII are 187.37, 187.66, and 186.02 for the three studies. The agreement of these results is not satisfactory. Because of the interference experienced when dimethyl ether was employed, we are convinced that the most reliable value is that obtained with methanethiol. The others are reported for the record.

Xylenes. The three xylenes were studied employing both methanethiol and dimethyl ether as reagents. The data obtained and the computed equilibrium constants are given in Tables VI–XI. Although there is some variation in each series of experiments, the equilibrium constants show an average deviation of about 10% or less. Since the free energies are small in all cases, the mean deviation in ΔG for the various reactions in no case exceeds 0.1 kcal/mol. When the proton affinities for the various xylenes determined from methanethiol and dimethyl ether are compared, a quite consistent difference of about 0.5 to 0.6 kcal/mol is observed. We are not certain why this discrepancy exists. It might, however, result from our assumptions concerning the need for path degeneracy. The average values for the three xylenes, as shown in Table XII, are in quite close agreement, the maximum difference being 0.11 kcal/mol between *p*-xylene and *m*-xylene. It seems doubtful that the difference is significant, and we are inclined to think that our measurements of the proton affinities of the xylenes in the gas phase are essentially equal.

It should be recalled that all of the values for toluene and the xylenes are referred to the proton affinity of methyl ether of 187 ± 1 kcal/mol as determined by Haney and Franklin.[6] We hope ultimately to obtain a more accurate absolute value for these proton affinities, but at this time suitable data do not exist. As a result, the uncertainties that we record are largely influenced by the estimated uncertainty in the proton affinity of methyl ether.

Table XII summarizes the results obtained in this study. It is of interest that the proton affinities are in the order that would be expected from studies of the basicity of the methyl benzenes as determined in solution by several authors and reported in Bronwer, Mackor and Maclean.[13] In fact, if we compute the difference in proton affinities from the quoted basicity constants employing the temperatures used in our instrument, we get the results given in Table XIII. It is interesting that although we no not get precise quantitative agreement, the discrepancies are not very great and the results are in

Table XIII. Comparison of Gas Phase and Solution Results

	Log $K_B{}^a$	Proton affinity, kcal/mol From soln[a,b]	This study
Benzene	−9.2	178.0	178.0
Toluene	−6.3	182.6	187.4
p-Xylene	−5.7	183.5	188.0
o-Xylene	−5.3	184.2	188.0
m-Xylene	−3.2	187.5	188.1

[a] From ref 13. [b] Assuming PA(C_6H_6) = 178.

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the same order, even including the order of the proton affinities of the three xylenes.

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Electronic Structure and Properties of Krypton Difluoride

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Abstract: *Ab initio* calculations have been performed on the linear symmetric configuration of KrF_2, using a 993-configuration "first-order" wave function and an extended basis set of Slater functions. These calculations yield a bound potential curve with respect to three infinitely separated atoms; the Kr–F bond distance is 1.907 Å and the dissociation energy is 0.39 eV, as compared to the experimental values of 1.889 ± 0.01 Å and 1.013 eV, respectively. A potential maximum is found at Kr–F distance 2.42 Å, lying 0.22 eV above the dissociation limit. The electric field gradient at the Kr nucleus, near the potential minimum, is very near the self-consistent field (SCF) value for an isolated Kr^+ ion but drops rapidly to zero near the potential maximum. These results show that the Kr–F bond is ionic in nature near the equilibrium separation and becomes covalent at larger separations, as proposed by Coulson. In contrast to the "first-order" wave function results, one configuration SCF calculations yield an attractive potential curve with a minimum at 1.813 Å and 2.98 eV *above* the SCF energy of three separated atoms. This behavior is permitted because the one-configuration SCF wave function does not dissociate to neutral separated atoms. However, two-configuration SCF calculations which allow proper dissociation to neutral separated atoms yield a repulsive potential curve with an *inflection point* near 1.85 Å. CI calculations using the two-configuration SCF occupied orbitals and including all eight valence shell configurations yield results quantitatively similar to the two-configuration SCF results. In addition, a series of SCF calculations has been carried out to study the importance of polarization functions. The results indicate that 4d functions centered on Kr are much less important than suggested by minimum basis set calculations. Finally, Koopmans' theorem ionization potentials are compared with the experimental photoelectron spectrum.

The chemistry of krypton centers about KrF_2,[2a] since most of the interesting xenon compounds (*e.g.*, XeF_4, XeF_6, and XeO_4) appear to have no stable krypton analogs.[2b] We have previously[3] studied KrF[4] and KrF^+ [5] by *ab initio* theoretical methods; the only other well-characterized krypton-containing molecule is the ionic $[KrF^+][Sb_2F_{11}]$ recently synthesized and characterized (by its Raman spectrum) by McKee and Bartlett.[6]

The only previous nonempirical quantum mechanical treatment of KrF_2 is that of Collins, Cruickshank, and Breeze,[7] who carried out a self-consistent field (SCF) calculation using a minimum basis set. The stated purpose of this calculation[7] was to investigate the importance of 4d basis functions in the electronic structure of KrF_2. However, recent work with extended basis sets[8] on the second-row hydrides SiH_4, PH_3, and H_2S showed that minimum basis set studies[9] greatly overestimated the importance of 3d functions in these molecules. We have used an extended basis set to study the effects of different types of "polarization" functions[10] within the SCF approximation.

Electron correlation[11,12] has been investigated using "first-order" wave functions, which have proven quite effective[13] in predicting the dissociation energies and geometries of simple molecules. KrF_2 provides an important test for any theoretical approach which attempts to properly treat electron correlation, since the molecule lies on the fringe of stability. A number of molecular properties are reported. These properties are obtained using the "first-order" wave functions and also wave functions of lesser accuracy.

The "first-order" wave function as we use the term here does not include all of the configurations which would appear in the first-order Schroedinger perturbation theory wave function. The sense of our use of the term has been described elsewhere.[13] Later in the

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