BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (7), 2167—2168 (1978)

Reactivity of Organic Ions by Chemical Ionization Mass Spectrometry. II. Chemical Ionization Mass Spectra of Alkylbenzenes with Methane by Using a Quadrupole Mass Spectrometer

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(Received September 13, 1977)

Synopsis. The titled spectra have been determined at 75 °C. The $(M+H)^+$ ion intensities for methylbenzenes decrease linearly with the number of methyl substituents. The $(M+H)^+$ ion intensities for dialkylbenzenes decrease in the order *o*->*m*->*p*-, while those of trimethylbenzenes decrease in the order 1,2,3->1,3,5->1,2,4-, and those of tetramethylbenzenes decrease in the order 1,2,3,4->1,2,3,5->1,2,4,5-.

In the previous paper the author reported chemical ionization mass spectra (CIMS) of alkylbenzenes with isobutane as reactant gas.[1] The result has been interpreted as showing that the order of the $(M+H)^+$ ion intensities of alkylbenzenes is dependent on the basicities of these compounds.

Since the $C_2H_5^+$ ion from methane is a stronger Brønsted acid than the *t*-$C_4H_9^+$ ion from isobutane,[2] in the case of methane some different results can be expected. No study has been reported on the CIMS of alkylbenzenes with three isomers with methane except that on diethylbenzenes by Munson and Field.[3] Methylbenzenes are suited for the study of the relationship between the number of methyl groups and the ion intensity of the formed ions, because of their small dealkylation.

The purpose of this paper is to explore the difference of reactivity due to the difference of properties between the two reactant gases.

Experimental

The mass spectra were measured with a Finnigan Model 3000 GC mass spectrometer which has been modified to operate under chemical ionization conditions.[1] The experimental conditions are the same as those used previously, which were as follows: ion source pressure, 1 mmHg; ion source temperature, 75 °C; electron energy, 90 eV. Low boiling samples were admitted to the ion source with a Nupro bellows metering valve SS-4BMG. High boiling and solid samples were admitted with the solid probe equipped with a heater. All values used in this work are the average of more than three measurements.

Methane (99.7%) obtained from Tokyo Methane Co., Ltd. was employed without further purification as the reagent gas. The following alkylbenzenes (Tokyo Kasei Kogyo Co., Ltd., extra pure or more) were studied: benzene (B), toluene(T), xylenes(X), ethyltoluenes(ET), diethylbenzenes(DEB), diisopropylbenzenes(DIPB), trimethylbenzenes(TrMB), tetramethylbenzenes(TeMB), pentamethylbenzene(PMB), and hexamethylbenzene(HMB).

TABLE 1. CIMS OF BENZENE AND HEXAMETHYLBENZENE (CH_4 REACTANT = 1 mmHg)

Benzene		Hexamethylbenzene	
Ion	RI(%Σ)[a]	Ion	RI(%Σ)[a]
$(M-15)^+$		$(M-15)^+$	2.7±0.3
$(M-1)^+$		$(M-1)^+$	25.8±0.4
M^+	5.1±0.2	M^+	18.0±0.4
$(M-1)^+$	79.9±0.3	$(M+1)^+$	42.1±0.3
$(M+29)^+$	5.5±0.1	$(M+29)^+$	3.1±0.0
$(M+41)^+$	1.6±0.0	$(M+41)^+$	0.6±0.1

a) Average of four replicates±average deviation.

Results and Discussion

Table 1 shows the reproducibility of the intensities for benzene and hexamethylbenzene. Such a good reproducibility is adequate for the purpose of this study. The spectra of 21 alkylbenzenes with methane are given in Table 2. The intensities of $(M+H)^+$ ions tend to decrease from benzene to *p*-diisopropylbenzene as the number of alkyl carbon atoms in the aromatic molecule increases. For methyl-substituted compounds there is a decrease in intensity of $(M+H)^+$ ions with increasing the number of methyl substituents on the benzene ring, that is, the protonated hydrocarbons decrease with increasing electron density on the benzene ring. These results are not consistent with those of usual chemical reactions and of reactions with isobutane. The $(M+H)^+$ intensities of dialkylbenzenes decrease in the order *o*->*m*->*p*-, while those of trimethylbenzenes decrease in the order 1,2,3->1,3,5->1,2,4,-, and those of tetramethylbenzenes decrease in the order 1,2,3,4->1,2,3,5->1,2,4,5-. These orders also are not the same as those obtained with isobutane.

As shown in Table 2, the $(M-H)^+$ ion intensities tend to increase from toluene to *p*-diethylbenzene with increasing the carbon number of the side chain. The $(M-H)^+$ intensities for methylbenzenes also increase with the methyl substituents on the benzene ring. The intensities of $(M-H)^+$ ions increase in the order *o*-<*m*-<*p*- in the disubstituted compounds, 1,2,3-<1,3,5-<1,2,4- in the trimethylbenzenes, and 1,2,3,4-<1,2,3,5-<1,2,4,5- in the tetramethylbenzenes. The order of the $(M-H)^+$ ion intensities for all the isomers is obviously opposite to that of the $(M+H)^+$ ion intensities.

As can be seen from Table 2, the intensities of $(M+29)^+$ ions for toluene, xylenes, ethyltoluenes, diethylbenzenes, and trimethylbenzenes are higher than that of benzene. This seems to be a result of the hyperconjugation effect due to the alkyl groups. On the contrary, the intensities of the $(M+29)^+$ ions for the compounds which have four or more methyl substituents are lower than that of benzene, and decrease

Table 2. CIMS (CH_4 reactant = 1 mmHg), RI (%Σ) of ions in alkylbenzenes

	$(M-43)^+$	$(M-41)^+$	$(M-29)^+$	$(M-15)^+$	$(M-1)^+$	M^+	$(M+1)^+$	$(M+29)^+$	$(M+41)^+$
B						5.1	79.9	5.5	1.6
T					3.9	5.1	74.5	7.1	1.9
o-X				1.2	6.1	5.4	69.7	8.0	1.9
m-X				1.2	8.0	5.4	68.7	7.6	2.0
p-X				1.2	10.6	6.0	66.7	6.9	1.6
o-ET				4.3	6.5	5.1	60.5	8.7	2.5
m-ET				4.3	8.1	5.7	59.6	7.3	2.4
p-ET				5.3	11.3	5.4	57.8	6.5	1.6
o-DEB	1.2	0.9	4.1	6.7	8.2	5.8	51.2	6.8	1.8
m-DEB	1.2	0.8	3.2	6.5	9.7	6.9	50.1	6.2	1.8
p-DEB	1.4	0.8	3.3	7.7	11.4	6.7	46.9	7.0	1.7
m-DIPB	2.3	16.5	2.8	9.1	6.7	3.2	19.1	0.3	0.6
p-DIPB	3.0	19.6	1.1	11.9	9.3	4.3	18.7	0.3	0.6
1,2,3-TrMB				1.4	10.0	5.9	66.9	6.5	1.8
1,3,5-TrMB				1.3	13.1	6.3	62.7	7.1	1.9
1,2,4-TrMB				1.4	14.7	6.5	62.4	6.4	1.5
1,2,3,4-TeMB				1.7	15.6	8.1	59.1	4.3	1.2
1,2,3,5-TeMB				1.8	19.7	8.9	56.4	4.9	1.1
1,2,4,5-TeMB				1.8	21.3	9.8	53.7	4.7	0.9
PMB				2.4	23.5	13.2	48.7	4.2	0.7
HMB				2.7	25.8	18.0	42.1	3.1	0.6

with the methyl substituents. This decrease results from the steric hindrance due to the methyl substituents. There is also a nearly similar tendency for the $(M+41)^+$ ions. Both $(M+29)^+$ and $(M+41)^+$ ions formed in all compounds in contrast with the $(M+57)^+$ ion observed in the case of isobutane; this can be explained on the basis of the differences of ionic volume.

The relationship between the $(M+H)^+$ ion intensities and the number of methyl substituents is different from the results with isobutane; this can be ascribed to the difference of Brøsted acid strength between the ion from methane and the ion from isobutane. The ion from methane is $C_2H_5^+$, which is a stronger Brønsted acid than t-$C_4H_9^+$ from isobutane,[2] so the $C_2H_5^+$ ion is both a stronger proton addition and hydride abstraction reactant than t-$C_4H_9^+$.[2] Actually the $(M+H)^+$ ion intensity of benzene is higher than that with the isobutane,[1] and the $(M-H)^+$ ion intensities of tetramethylbenzenes are higher than those with the isobutane.[1] The attack by a strong acid, such as $C_2H_5^+$ ions, is not appreciably affected by the basicity of aromatics in contrast with the attack by the weaker acid of t-$C_4H_9^+$ ions. Therefore, in this case, the basicity for the aromatics is not necessary for the proton addition. Since the $C_2H_5^+$ ion can abstract hydride in proportion to the number of methyl substituents, as described above, because of its strong acidity, the formation of $(M+H)^+$ ion is affected rather by the formation of the $(M-H)^+$ ion than the basicity of aromatics. That is to say, in the proton addition reaction, a strong Brønsted acid, such as the $C_2H_5^+$ ion, counteracts any effect resulting from the electron density on the benzene ring. Accordingly, in the case of a methane reactant, the order of the proton addition reactions is not consistent with the order of the basicities for alkylbenzenes.

In spite of the higher basicity of *m*-xylene compared with *o*-xylene,[4] the $(M+H)^+$ intensity for *m*-xylene is lower than that for *o*-xylene, which is opposite to the result with isobutane.[1] This discrepancy also may be explained in the same way as ascribed above: that is, in the case of a methane reactant, the formation of $(M+H)^+$ is affected rather by the formation of $(M-H)^+$ ion than by the basicity of aromatics. However, in this case, while each xylene has the same methyl number, the reason why the hydride is easily abstracted from *m*-xylene is not known at present. Thus, it can be considered that the stability of the ions can not be determined only from the order of formation for the ions, for that order depends on the kind of reactant gas. The alkylbenzene isomers can be identified by the exchange of reactant gas.

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