On-Line Monitoring of the Photolysis of Benzyl Acetate and 3,5-Dimethoxybenzyl Acetate by Membrane Introduction Mass Spectrometry

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Membrane introduction mass spectrometry (MIMS) allows on-line monitoring of the products of photolysis (254 nm) of benzyl acetate in aqueous methanol and 3,5-dimethoxybenzyl acetate in water. The reaction mixture is continuously exposed to a silicone membrane through which analyte molecules permeate into a triple quadrupole mass spectrometer for qualitative and quantitative analysis. Ionization is achieved by either isobutane or ammonia chemical ionization, and ions characteristic of the reactant ester and its products are monitored simultaneously and continuously. Three products, benzyl methyl ether, ethylbenzene, and bibenzyl are observed in the benzyl acetate photolysis. Two products, 3,5-dimethoxybenzyl alcohol and 3,5-dimethoxyethylbenzene, are formed in the photolysis of 3,5-dimethoxybenzyl acetate. Quantitation is achieved through calibration using external standard solutions and, in the case of benzyl methyl ether, tandem mass spectrometry is used to verify product identification. During the photolysis of benzyl acetate, benzyl methyl ether and ethylbenzene are produced at onset with similar efficiencies. For the 3,5-dimethoxy ester photolysis, performed in aqueous solution, the efficiency of formation of the polar product 3,5-dimethoxybenzyl alcohol is about 300 times greater than that of the nonpolar product 3,5-dimethoxyethylbenzene. The results show that the relative reaction rates are dependent on the solvent and on the photon intensity and are consistent with earlier off-line experiments by Pincock *et al.* which showed that the photolysis proceeds through both ion and radical pair intermediates. To the best of our knowledge, the work reported here describes the first analysis of the photochemistry of an aralkyl ester in water and the first use of on-line mass spectrometry in a mechanistic study.

Introduction

Little is known about the photochemistry of organic compounds in water because their low solubility makes characterization of products and determination of their yields difficult. Also, the usual method used to follow the kinetics of such reactions involves collection of aliquots at chosen time intervals during the reaction and their off-line analysis by the use of gas chromatography or other spectroscopic techniques.[1] These methods, however, are time-consuming and do not allow real time on-line monitoring of the photolysis process. Because there appear to be no studies in the literature in which on-line monitoring is used in order to perform mechanistic investigations by mass spectrometry (although reports on the monitoring of intermediates in bioreactors have appeared[2]), we were intrigued by the possibility that MIMS (membrane introduction mass spectrometry)[3] could be used for continuously monitoring such reactions. Recent advances in MIMS, especially the use of the direct insertion membrane probe, used in conjunction with flow injection analysis procedures of sampling, provide the short response times which are desirable for on-line reaction monitoring. The importance of the experiment is that the method of detection, mass spectrometry, is a universal method, and hence a suit of compounds can be examined simultaneously over the entire reaction period.

Membrane introduction mass spectrometry is a rapid, rugged, analytical method which has been applied to the on-line monitoring of volatile organic compounds (VOC's) in water and air,[4] to *in vivo* analysis of VOC's in blood,[5] to characterization of fermentation products,[6] and to monitoring such processes as wastewater treatment.[7] A semipermeable membrane, usually a silicone polymer, acts as an interface between the sample solution and the vacuum of the mass spectrometer. The hydrophobic membrane is permeable to relatively nonpolar and low molecular weight compounds while the aqueous matrix is excluded. Analyte molecules permeate the membrane by the process of pervaporation[8] and are then ionized. The high resistance to fouling, and the mechanical and chemical resistance of silicone membranes, adds to their usefulness.

Most organic photochemical reactions involve only radical intermediates, and, to a first approximation, the polarity of the solvent is not expected to be a critical

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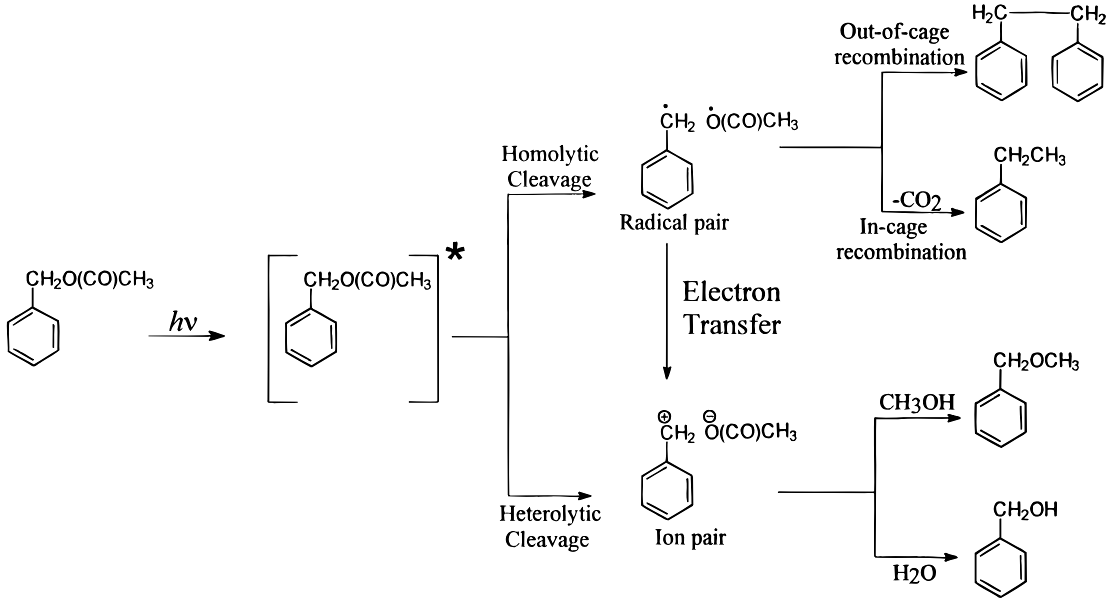
Scheme 1. General Mechanism for the Photolysis of Benzyl Acetate in Methanol−Water



factor in the reaction. However, some photochemical reactions do involve ionic intermediates and, most interestingly, some involve reaction pathways where both radical and ionic species are important. The unique properties (dielectric constant, viscosity) of water as a solvent could therefore have significant mechanistic effects. Recently, extensive results on the photochemistry of arylmethyl esters in methanol have been reported.[1,9,10] The general conclusion from these studies, as outlined in Scheme 1, is that the excited state of the ester reacts to give a radical pair by homolytic cleavage. Direct heterolytic cleavage to an ion pair is not a major pathway. Instead, the ion pair is formed by an electron transfer process in the radical pair. The rate of this process, according to Marcus's theory[11] of electron transfer, is dependent on the reorganization energy. The solvent component of this energy will undergo large changes as the dielectric constant of the solvent changes, hence the expectation that the distribution of reaction products should be dependent on the choice of solvent.

The objective of this work is, therefore, to explore the application of the MIMS method for the on-line monitoring of the photolysis of benzyl acetate in methanol−water and 3,5-dimethoxybenzyl acetate in water. For the unsubstituted ester, the solubility in water alone was low and 1:1 (v/v) methanol−water was used. The expected reaction intermediates (Scheme 1) are a radical pair and an ion pair. For the radical pair, decarboxylation and in-cage coupling gives ethylbenzene and carbon dioxide. Out-of-cage dimerization of the benzyl radical gives bibenzyl. For the ionic intermediate, trapping by methanol when it is the solvent gives benzyl methyl ether, but when water is the solvent, benzyl alcohol is produced.

Experimental Section

A solution of 400 mg/L benzyl acetate in 1:1 methanol−water or 3,5-dimethoxybenzyl acetate in water in an 8 mL quartz tube was irradiated in a Rayonet photoreactor at a wavelength of 254 nm. The solution was recirculated *via* Teflon transfer lines to a direct-insertion membrane (silicone) probe[12] by a peristaltic pump at 1 mL/min. The probe was inserted directly into the ion source of a triple quadrupole mass spectrometer and was heated to 80 °C. Analytes permeating the membrane were chemically ionized by either isobutane or ammonia at an estimated pressure of 0.5 torr. External calibration was achieved by flow injection of 500 mL aliquots of either sample or standard solution through the membrane probe. Data were acquired by scanning from *m/z* 70 to 330 in 2 s. Benzyl acetate, benzyl alcohol, ethylbenzene, and bibenzyl were obtained commercially while benzyl methyl ether, 3,5-dimethoxybenzyl acetate, 3,5-dimethoxybenzyl alcohol, and 3,5-dimethoxyethylbenzene were synthesized by published methods.[1,13]

Results and Discussion

Photolysis of Benzyl Acetate in Methanol−Water. Mass spectra due to individual compounds must be known in order to interpret data on reaction mixtures. Table 1 summarizes the abundances of the major ions in the mass spectra recorded by MIMS using isobutane CI for aqueous methanol (1:1) solutions of benzyl acetate, benzyl methyl ether, benzyl alcohol, ethylbenzene, and bibenzyl. The concentrations were 100 mg/L each, except that for benzyl alcohol a concentration of 1000 mg/L was used. All the mass spectra show a common fragment ion at *m/z* 91, due to the benzyl group, and also the protonated molecule $[M + H]^+$, except that benzyl alcohol shows the $[M\text{-}H]^+$ ion. On the basis of this information, the $[M + H]^+$ ions were chosen to monitor the compounds, except that the concentrations of benzyl alcohol and ethylbenzene could not be measured directly with this reagent gas, because both give the same characteristic ion, *m/z* 107. Differentiation between these two compounds was achieved by changing the CI reagent gas to ammonia (all subsequent experiments used this reagent, see below). Although tandem mass spectrometry (MS/MS) could have been used to differentiate these two compounds, the choice of another CI reagent gas is

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Table 1. Relative Peak Intensities in Isobutane and Ammonia CI Mass Spectra of Methanol−Water (1:1) Solutions of Benzyl Acetate, Benzyl Methyl Ether, Benzyl Alcohol, Ethylbenzene, and Bibenzyl. Characteristic Ions Used for Monitoring Are Marked with an Asterisk

	mass spectral peaks with relative intensity in parenthesis	
sample (MW)	isobutane CI	ammonia CI
benzyl acetate (150)	82 (5%), 85 (11%), 91 (100%), 93 (7%), 151* (40%)	90 (1%), 91 (2%), 108 (13%), 128 (1%), 168* (100%), 169 (8%)
benzyl methyl ether (122)	81 (3%), 85 (1%), 91 (100%), 92 (4%), 93 (2%), 123* (39%)	91 (7%), 108 (14%), 121 (8%), 122 (13%), 140* (100%), 141 (8%)
benzyl alcohol (108)	91 (100%), 92 (8%), 105 (3%), 107* (18%), 108 (7%), 109 (1%)	91 (22%), 94 (8%), 108 (75%), 109 (6%), 126* (100%), 127 (8%)
ethylbenzene (106)	65 (100%), 75 (2%), 89 (1%), 105 (2%), 106 (10%), 107* (75%), 108 (2%)	82 (3%), 91 (100%), 105 (5%), 106* (20%), 107 (1%)
bibenzyl (182)	91 (6%), 99 (6%), 105 (90%), 112 (9%), 181 (21%), 182 (3%), 183* (100%), 184 (4%)	87 (24%), 91 (38%), 108 (66%), 128 (5%), 200* (100%), 201 (2%)

preferred because it allows data to be taken at a greater rate than would the MS/MS experiment.

Photolysis, using a low UV light intensity (two lamps in a Rayonet photoreactor), of a water−methanol (1:1) solution of benzyl acetate with continuous monitoring of the reaction mixture gave the results that the ion abundance at *m/z* 151 (benzyl acetate, $[M + H]^+$) decreases with time while the abundance of *m/z* 123 (benzyl methyl ether, $[M + H]^+$) shows a corresponding rise with time. The ion at *m/z* 183 (bibenzyl, $[M + H]^+$) has a very low abundance indicating that this is a very minor product. Possible isomers of benzyl methyl ether are 2-phenylethanol and phenyl ethyl ether. The protonated 2-phenylethanol will undergo H_2O loss to give an ion at *m/z* 105 while the protonated phenyl ethyl ether will lose C_2H_4 to give an ion at *m/z* 95 upon collision-induced dissociation.[14] In addition, isobutane CI of 2-phenylethanol gives a characteristic ion at *m/z* 122 ($M^{+\bullet}$), hence the possibility of *m/z* 123 being 2-phenylethanol is excluded. The ion at *m/z* 123 was allowed to undergo collision-induced dissociation (CID) with argon (17 eV). The product ion spectrum of *m/z* 123 from the photolyzed solution displays two peaks, *m/z* 91 (100%) and *m/z* 123 (63%), consistent with the results for a standard solution of benzyl methyl ether. Thus, the ion at *m/z* 123 was unambiguously identified as the protonated benzyl methyl ether.

Quantitation was achieved by calibration using external standard solutions based on peak area of the ion chromatograms calculated using the data system of the instrument. The concentrations of benzyl acetate and benzyl methyl ether were found to be 35 and 28 mg/L, respectively, in this photolysis after 50 min. This corresponds to a yield of 9.4% of benzyl methyl ether at a 91% conversion of benzyl acetate. (Note that these values do not consider losses at the membrane and so the calculated yield represents a lower limit, see below.) The isomer, 2-phenylethanol, which yields a characteristic ion at *m/z* 122 ($M^{+\bullet}$) under isobutane CI conditions, is a significant product (26%) in methanol photolysis,[1] but is not observed in methanol−water. Subsequent experiments were similar, but two changes were made. First, ammonia was used exclusively as the CI reagent gas. Second, a high UV light intensity (13 lamps) was used in an attempt to increase the yield of the product bibenzyl. Table 1 summarizes the relative ion abundances in the ammonia CI mass spectra of standard aqueous methanol (1:1) solutions of benzyl acetate, benzyl methyl ether, benzyl alcohol, ethylbenzene, and bibenzyl when examined by MIMS. Note that benzyl alcohol and benzyl methyl ether have different characteristic ions under ammonia CI conditions and hence they can now be differentiated. Under ammonia CI, benzyl alcohol gives characteristic ions of *m/z* 109 ($[M + H]^+$) and 126 ($[M + NH_4^+]$) while ethylbenzene has a characteristic ion of *m/z* 106 ($M^{+\bullet}$). Detection limits (S/N = 3) of benzyl acetate, benzyl methyl ether, bibenzyl, ethylbenzene and benzyl alcohol in 1:1 methanol−water solution were determined as 5.0, 2.0, 2.0, 10, and 50 mg/L, respectively. Figure 1 shows the abundances of ions characteristic of benzyl acetate (*m/z* 168, $[M + NH_4^+]$), benzyl methyl ether (*m/z* 140, $[M + NH_4^+]$), bibenzyl (*m/z* 200, $[M + NH_4^+]$), and ethylbenzene (*m/z* 106, $M^{+\bullet}$) as a function of time. Note that the photolysis started at scan number 50 and that it takes approximately 1 min more for the solution to flow from the photochemical reactor to the mass spectrometer.

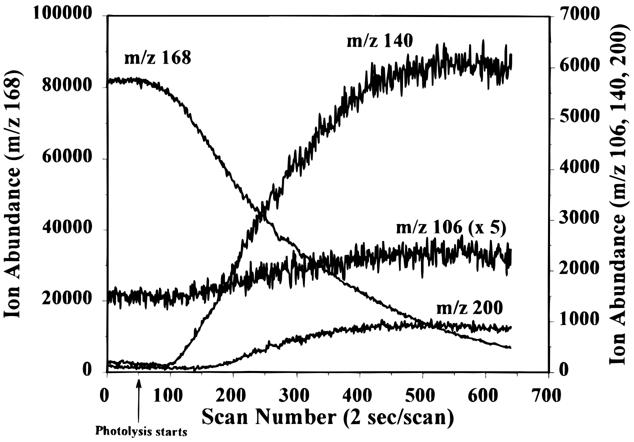

Figure 1. The ion abundance of benzyl acetate (*m/z* 168, $[M + NH_4^+]$), benzyl methyl ether (*m/z* 140, $[M + NH_4^+]$), bibenzyl (*m/z* 200, $[M + NH_4^+]$), and ethylbenzene (*m/z* 106, $M^{+\bullet}$) are plotted as a function of time under ammonia CI condition. Note the ion abundance at *m/z* 106 is expanded 5 times. The photolysis started at scan number 50. Ion abundances have not been corrected for losses through the membrane; this procedure changes the ion counts but has an insignificant effect on the shapes of the curves.

There is no signal due to the ions which are characteristic of benzyl alcohol, *m/z* 109 and 126, throughout the whole photolysis period, indicating that benzyl alcohol is not formed in significant quantities under these conditions. The ion abundance of benzyl methyl ether started to increase at scan number 90 as did that of ethylbenzene and bibenzyl although the low sensitivity to ethylbenzene and the low rate of formation of bibenzyl, a bimolecular reaction product, make their onsets more difficult to locate. The low sensitivity for ethylbenzene is due to the difficulty of protonation under ammonia CI conditions since its proton affinity (191.6 kcal/mol) is

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[14] Sigsby, M. L.; Day, R. J.; Cooks, R. G. *Org. Mass Spectrom.* **1979**, *14*, 273.

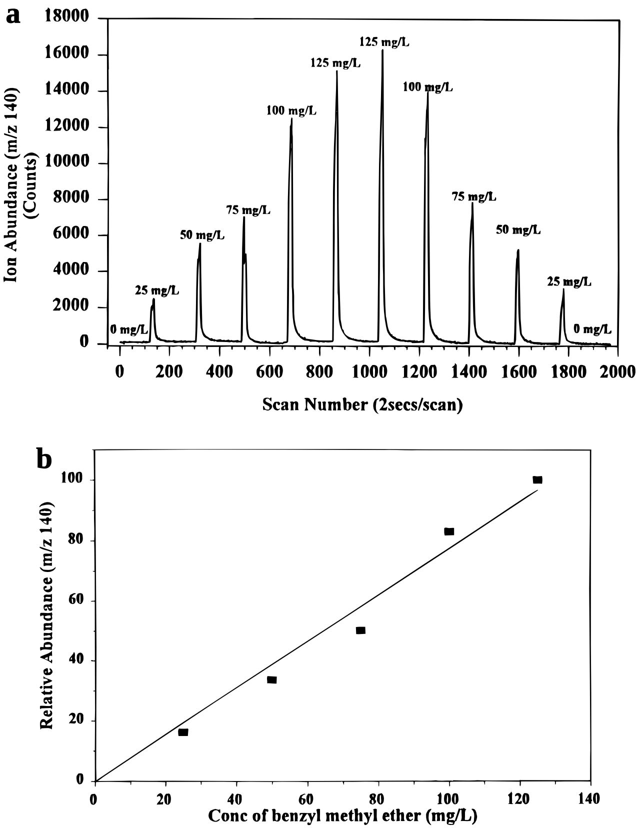

Figure 2. (a) Calibration scans for benzyl methyl ether under ammonia CI conditions. (b) Least squares fit of the calibration.

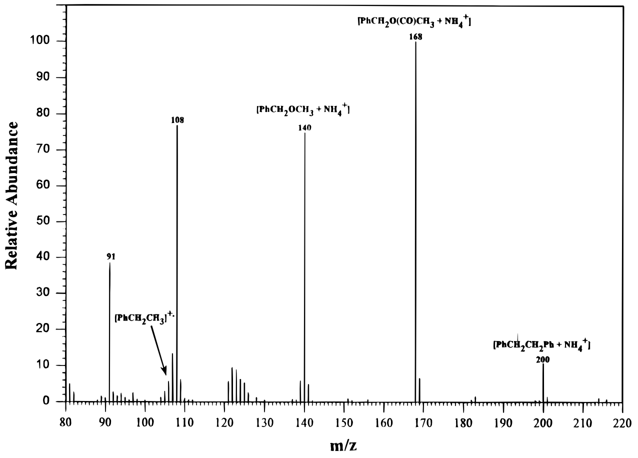

Figure 3. An ammonia CI mass spectrum of the benzyl acetate solution after photolysis for 20 min.

lower than that of ammonia (204.0 kcal/mol).[15] Figure 2a shows calibration results for benzyl methyl ether, *m/z* 140, and Figure 2b shows the least squares fit to a set of calibration data. The precision of the experiment is represented in these results.

Figure 3 shows the ammonia CI mass spectrum of the solution after photolysis for about 20 min. Characteristic peaks show the presence of ethylbenzene (*m/z* 106, $[PhCH_2CH_3]^{+\bullet}$), benzyl methyl ether (*m/z* 140, $[PhCH_2OCH_3 + NH_4^+]$), benzyl acetate (*m/z* 168, $[PhCH_2O(CO)CH_3 + NH_4^+]$) and bibenzyl (*m/z* 200, $[PhCH_2CH_2Ph + NH_4^+]$). Other prominent ions, such as *m/z* 91 and 108, are due to contributions from several compounds (Table 1). The concentrations of benzyl acetate, benzyl methyl ether, bibenzyl, and ethylbenzene were found to be 32, 44, 7.6, and 32 mg/L, respectively, after about 20 min of photolysis. These measurements were made by calibration using external standard solutions; they correspond to 92% conversion of benzyl acetate and the corresponding yields of benzyl methyl ether, ethylbenzene, and bibenzyl are 15%, 12%, and 3.4%, respectively. Note that the ethylbenzene data are the least precise because of the low abundance of the characteristic ion, *m/z* 106. It is expected that benzyl alcohol should be formed in a yield comparable to that of benzyl methyl ether (44 mg/L). However, the detection limit for benzyl alcohol is only 50 mg/L, so it is not observed. A separate off-line photolysis experiment was performed under static conditions with product analysis being made only at the end of the reaction period and hence no reagent loss being possible. Note that under these more sensitive conditions, a small signal was observed due to the ion $[PhCH_2OH + NH_4^+]$, characteristic of benzyl alcohol, indicating that benzyl alcohol is indeed formed during the photolysis. Previous off-line experiments in methanol solvent showed yields of 26%, 19%, and 23%, for benzyl methyl ether, ethylbenzene, and bibenzyl, respectively, together with other products in a total 94% yield.[1] The difference in relative yields between the on-line aqueous/methanol and the off-line methanol experiments is simply ascribed to the increased polarity of the solvent which significantly reduces the formation of the nonpolar product bibenzyl.

The poor mass balance in the MIMS experiments is primarily due to analyte loss through the membrane as the solution is recirculated while the limited membrane permeability to the more polar compounds such as benzyl alcohol and 2-phenylethanol, both of which have similar detection thresholds, contributes to the errors in the mass balance. The loss of benzyl acetate through the membrane was investigated in a separate experiment in which a 400 mg/L benzyl acetate solution was aspirated through the membrane probe over the same period of time used for the photolysis reactions but with the UV light off. It was found that the signal due to benzyl acetate decreases steadily and eventually reached 60% of its initial value. Similar experiments were also performed to investigate analyte loss through the membrane for benzyl methyl ether, bibenzyl, and ethylbenzene. It was found that they show similar percentage losses, in the range of 35−45%, through the membrane. The fact that a linear relationship exists between the concentrations of the unimolecular reaction products (see Figures 4 and 7) is a further indication that the analyte losses do not differ significantly. In order to account quantitatively for the mass imbalance, we performed the following estimates. If we assume that the percentage loss is independent of concentration, the corrected yields of benzyl methyl ether, ethylbenzene, and bibenzyl are 25%, 20%, and 5.7% respectively, based on 40% analyte loss through the membrane. If benzyl alcohol is formed in a yield comparable to that of benzyl methy ether, then a total corrected yield of 76% is obtained. The remaining 24% may be partly due to 2-phenylethanol, which is formed in 26% yield in methanol photolysis,[1] which is not detected by MIMS due to the limited membrane permeability to this compound. The errors in analyte loss through the membrane can presumably be reduced by doing larger scale photolysis such that the losses are

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[15] Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

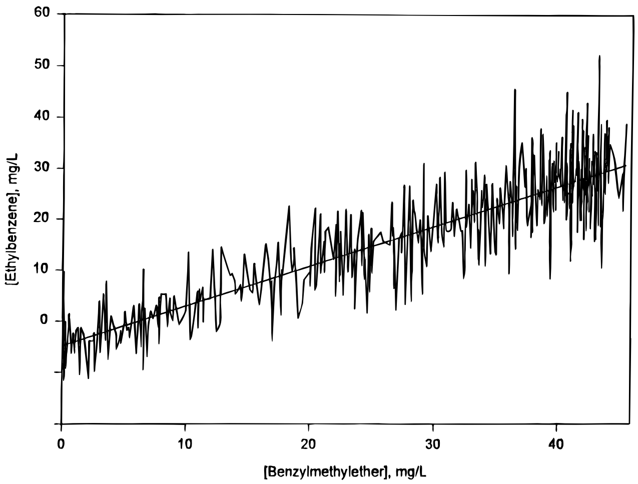

Figure 4. A plot of concentration of ethylbenzene versus the concentration of benzyl methyl ether. The slope, after correcting the concentration units to mol/L, gives the relative rate of formation of ethylbenzene with respect to benzyl methyl ether.

small compared to the volume of the reaction vessel. If corrections to the observed ion abundances shown in Figure 1 are made to account for losses of analyte through the membrane, only insignificant changes in the data are found; these results are therefore not reproduced.

Information on relative rates of product formation can be obtained by comparing initial rates of formation derived from the initial slopes in Figure 1, each of which is linear for the first few minutes. Note that the errors due to analyte loss are small at the beginning of the photolysis. The initial rates of formation of benzyl methyl ether, ethylbenzene, and bibenzyl were found to be in the ratio of 1:0.93:0.15. The threshold rate of formation of bibenzyl is about 1 order of magnitude slower than the rate of formation of ethylbenzene and benzyl methyl ether. The relative rate, after correcting concentration units to mol/L, can also conveniently be obtained by plotting the concentration of ethylbenzene against benzyl methyl ether, as shown in Figure 4. The ratio of the concentrations of the two products remains essentially constant (0.90) over the full photolysis period. This result is as expected for two products being formed from two competing pathways and indicates that they are both primary photoproducts.

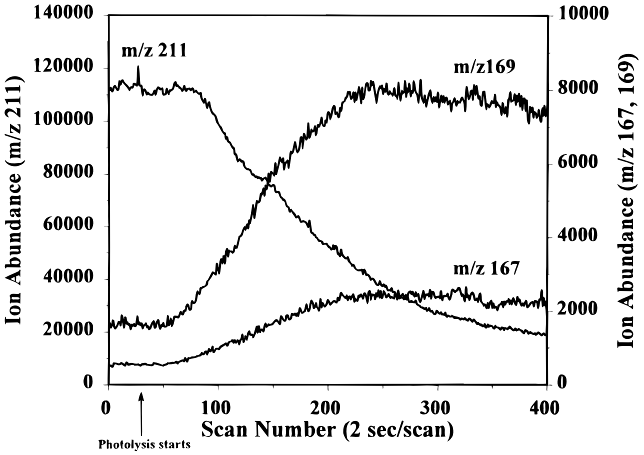

Figure 5. The ion abundance of 3,5-dimethoxybenzyl acetate (*m/z* 211, [M + H^+]), 3,5-dimethoxybenzyl alcohol (*m/z* 169, [M + H^+]), and 3,5-dimethoxyethylbenzene (*m/z* 167, [M + H^+]), plotted as a function of time under ammonia CI condition. The photolysis started at scan number 30.

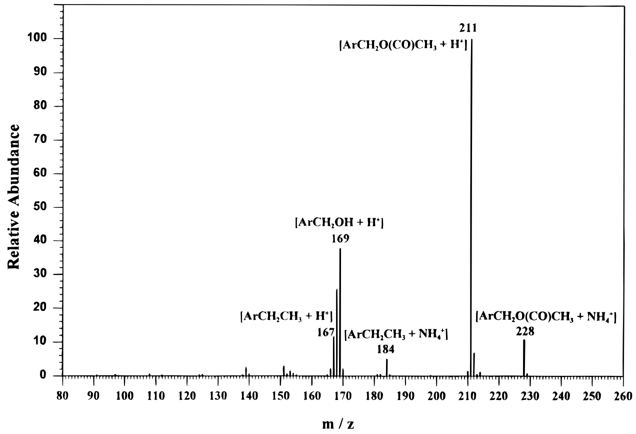

Figure 6. An ammonia CI mass spectrum of the 3,5-dimethoxybenzyl acetate solution after photolysis for about 12 min. The symbol Ar represents the 3,5-dimethoxyphenyl group.

Photolysis of 3,5-Dimethoxybenzyl Acetate in Water. When the solvent is changed to pure water, the methyl ether is no longer formed because the nucleophile CH_3OH is not present. Under ammonia CI conditions, the substituted acetate, the alcohol, ethylbenzene, and bibenzyl all give characteristic [M + H^+] ions which occur at *m/z* 211, 169, 167, and 303, respectively. The detection limits of 3,5-dimethoxybenzyl acetate, 3,5-dimethoxybenzyl alcohol, and 3,5-dimethoxyethylbenzene in water were determined as 5.0, 50, and 0.2 mg/L respectively. During photolysis at high UV light intensity (13 lamps), the reactants and products were monitored continuously. Figure 5 shows the intensities of ions characteristic of 3,5-dimethoxybenzyl acetate, 3,5-dimethoxybenzyl alcohol, and 3,5-dimethoxyethylbenzene as a function of time. Note that there is no signal due to the ion characteristic of the substituted bibenzyl (*m/z* 303, [M + H^+]). Since bibenzyl permeates readily through the membrane with a detection limit of 2 mg/L, the substituted bibenzyl is expected to permeate through the membrane, too, as the difference in volatility between the two compounds is not large. Its negligible formation is expected because this compound can only be formed by dimerization of benzyl radicals which have escaped from the solvent cage, which the high viscosity of water appears to prevent. Figure 6 shows the ammonia CI mass spectrum of the solution after photolysis for about 12 min. Characteristic peaks show the presence of 3,5-dimethoxyethylbenzene (*m/z* 167 and 184), 3,5-dimethoxybenzyl alcohol (*m/z* 169) and 3,5-dimethoxybenzyl acetate (*m/z* 211 and 228). Their concentrations were found to be 0.5, 174, and 6.6 mg/L, respectively, by calibration using external standard solutions. This corresponds to 98% conversion of the acetate and the corresponding yields of the alcohol and 3,5-dimethoxyethylbenzene are 55% and 0.2%. The loss of the alcohol through the membrane was also measured to be about 40%. If the analyte loss is also considered, as discussed above, the corrected yield of the alcohol is 92%. Since the alcohol is more polar than 3,5-dimethoxyethylbenzene, its relatively high yield is expected in the polar solvent. Information on relative rates of product formation can be obtained by comparing initial rate of formation derived from the initial slopes in Figure 5. The ratio of initial rates of formation of the alcohol and substituted ethylbenzene were found to be 319:1. The

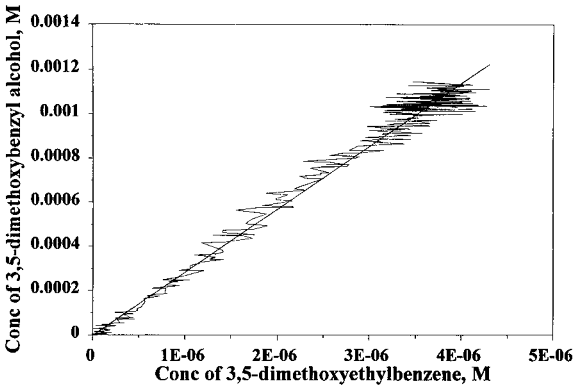

Figure 7. A plot of concentration of 3,5-dimethoxybenzyl alcohol versus the concentration of 3,5-dimethoxyethylbenzene (total time 12 min). The slope gives the relative rate of formation of 3,5-dimethoxybenzyl alcohol with respect to 3,5-dimethoxyethylbenzene.

relative rate can also conveniently be obtained by plotting the concentration of the alcohol against the substituted ethylbenzene, as shown in Figure 7. The ratio of the concentrations of the two products remains essentially constant (285:1) over the full photolysis period. The fact that the alcohol is formed about 300 times faster than the substituted ethylbenzene also indicates that solvent has a significant influence on the mechanism of this photochemical reaction.

Conclusions

The capability of performing on-line monitoring of photolysis reactions by mass spectrometry is shown for the first time and is used to investigate the mechanism of benzyl ester photolysis. Significantly, this capability is demonstrated to extend to the study of reactions in aqueous solution. The high selectivity of the experiment makes it a promising technique in studying relative rates of product formation, although improvements are needed in precision and sensitivity. These are likely to come as a wider range of membrane materials, more suitable than are silicone polymers to the compounds studied here, becomes available.

The results show that the relative photolysis rates are dependent on the solvent, and the observed products are consistent with earlier demonstrations by Pincock *et al.*[1,9,10] based on off-line experiments that the photolysis proceeds through both ion and radical pair intermediates. Obvious advantages of MIMS over the methods used previously for such studies are that MIMS is simple, it provides real time data during photolysis, and sample pretreatment, such as solvent extraction or other preconcentration procedures, is not needed.

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