J. Org. Chem. 1987, 52, 3099–3101

Effects of Additives on the Rates of Methoxymercuration of Para-Substituted Styrenes

Adolphus Lewis

Department of Chemistry, Howard University, Washington, D.C. 20059

Received September 10, 1986

The second-order rates of methoxymercuration for a series of para-substituted styrenes have been determined, at 25 °C, in the presence of varying amounts of 18-crown-6, CCl_4, and C_6H_{12}. Increasing the amount of each additive causes reductions in the values of k_2, with CCl_4 and C_6H_{12} exerting a larger effect than 18C6. In the presence of CCl_4 and C_6H_{12}, while the values of k_2 vary linearly with the MeOH concentration, for a given styrene and MeOH concentration they are virtually the same. In all cases, excellent linear plots of log k_2 vs. σ and σ^+ were obtained. The values of $-\rho$ and $-\rho^+$ are independent of the concentrations of the additives and the identity of the cosolvent. The results of this study, in conjunction with those of our previous study on the use of p-dioxane as an additive, lead us to conclude that complexation of the Hg^{2+} ions by 18C6, hence p-dioxane, has a smaller rate-retarding effect on this reaction than decreasing the polarity of the medium does.

Introduction

In our last paper[1] on the methoxymercuration of a series of para-substituted styrenes in the presence of various amounts of p-dioxane, we proposed that p-dioxane caused the observed rate reductions by two competing[2] pathways: [1] it caused a decrease in the solvating ability of the medium and [2] it formed a weak complex with Hg^{2+} ions present in solution. In order to evaluate the relative importance of these pathways, we determined the second-order rates of methoxymercuration for the same series of styrenes in the presence of varying amounts of carbon tetrachloride, cyclohexane, and 18-crown-6.

Carbon tetrachloride and cyclohexane were chosen because their dielectric constants (2.23 and 2.01, respectively) are essentially equal to p-dioxane's (2.21). Accordingly, since CCl_4 and C_6H_{12} are less polar than MeOH and they cannot form a complex with Hg^{2+} ions, any reduction in the values of k_2 observed in the presence of these additives can be attributed to the fact that they lower the polarity of the medium. Further, since CCl_4 and C_6H_{12} have similar dielectric constants, the values of k_2 for a given styrene in $MeOH/CCl_4$ and $MeOH/C_6H_{12}$ mixtures of the same MeOH concentration should be approximately the same. On the other hand, while CCl_4 and p-dioxane have the same dielectric constant, because of the proposed added effect of complexation of the Hg^{2+} ions by the latter, the values of k_2 in $MeOH/CCl_4$ and MeOH/p-dioxane mixtures of the same MeOH concentration should not be the same. Thus comparisons of the values of k_2 for each styrene in the presence of these three cosolvents should permit us to assess the effect of decreasing the solvent's polarity on the rates of this reaction. 18C6 was chosen because it is known to form complexes with cations[3] and because it could be used in such low concentrations that its effect on the polarity of the medium would be negligible. Thus comparisons of the values of k_2 for each styrene in the presence and absence of this compound should permit us to assess the importance of complexation of the Hg^{2+} ion by 18C6, hence p-dioxane, in this reaction.

Table I. Second-Order Rate Constants for Reaction of p-$XC_6H_4CH{=}CH_2$ with $Hg(OAc)_2$[a] in Various Solvents at 25 °C

	100k,[b] M^{-1} s^{-1} in solv[c]				
X	M[d]	MC	MCy	MD[d]	MCf
		21.1 M Mixtures			
MeO	11300	12600	11300	2800	
Me	1980	1550	1360	348	
H	417	315	268	88.8	
F	336	246	216	70.6	
Br	93.1	71.5	62.1	19.0	
CN	3.41	2.27	2.21	0.538	
NO_2	1.97	1.30	1.30	0.303	
		17.6 M Mixtures			
MeO		4520	5020	579	6570
Me		754	510	93.1	1430
H		149	133	18.9	272
F		129	112	14.8	213
Br		35.1	32.3	3.52	60.3
CN		1.11	1.30	0.117	1.39
NO_2		0.629	0.753	0.0705	0.827
		15.8 M Mixtures[e]			
MeO		3240	3210	318	
Me		553	430	32.0	
H		107	100	8.11	
F		87.2	86.5	6.17	
Br		23.6	25.2	1.74	
CN		0.737	0.978	0.0555	
NO_2		0.353	0.540	0.0287	

[a] The initial concentrations of the $Hg(OAc)_2$ solutions, as determined by titrations of stock solutions with KSCN, ranged from 0.0168 to 0.0178 M for all styrenes except p-methoxystyrene. For this compound, the concentrations ranged from 0.00250 to 0.00290 M. [b] The average of three or more determinations. The average uncertainty is ±2%. [c] Solvent designations: M = MeOH; MC = $MeOH/CCl_4$; MCy = $MeOH/C_6H_{12}$; MD = MeOH/p-dioxane; MCf = $MeOH/CHCl_3$. [d] Taken from ref 1. [e] A 16.8 M solution was used in the case of the $MeOH/C_6H_{12}$ mixture.

Results[4] and Discussions

The second-order rate constants, shown in Tables I and II, respectively, for the reaction of **1** with mercuric acetate

$$1 = p\text{-}XC_6H_4CH{=}CH_2$$

a, X = MeO; **b**, X = Me; **c**, X = H;
d, X = F; **e**, X = Br; **f**, X = CN; **g**, X = NO_2

in the presence of varying amounts of the cosolvents and

---

[1] Lewis, A. *J. Org. Chem.* **1984**, *49*, 4682.

[2] Nagy, O. B.; Wa Muanda, M.; Nagy, J. B. *J. Phys. Chem.* **1979**, *83*, 1961.

[3] (a) Fux, P.; Lagrange, J.; Lagrange, P. *J. Am. Chem. Soc.* **1985**, *107*, 5927. (b) Liesegang, G. W.; Farrow, M. M.; Vazquez, F. A.; Purdie, N.; Eyring, E. M. *Ibid.* **1977**, *99*, 3240.

[4] The results reported herein were obtained by using a linear least-squares program on a computer. All correlation coefficients were 0.993 or better.

0022-3263/87/1952-3099$01.50/0

Table II. Second-Order Rate Constants for the Reaction of p-$XC_6H_4CH{=}CH_2$ with $Hg(OAc)_2$[a] in the Presence of 18-Crown-6 Ether at 25 °C

X	$100k_2$,[b] $M^{-1}\ s^{-1}$ in mM 18C6 1.81	3.03	6.02	9.03
MeO	3650	2820	1910	1460
Me	449	361	261	222
H	97.8	80.4	64.8	59.2
F	76.0	63.7	49.4	44.2
Br	23.4	19.8	16.4	15.6
CN	0.939	0.838	0.777	0.807
NO_2	0.555	0.507	0.463	0.487

[a] The initial concentration of the $Hg(OAc)_2$ solutions, as determined by titrations of stock solutions with KSCN, was 0.0179 M. [b] The average of three or more determinations. The average uncertainty is ±2%.

18C6 were determined as previously described by us.[5] The methanol concentrations of the $MeOH/CCl_4$ mixtures used were 21.1 M, 17.6 M, and 15.8 M. These concentrations were chosen because they are the same as those used in our[1] MeOH/p-dioxane mixtures. Cyclohexane's solubility in methanol is limited; thus a 16.1 M mixture was used instead of the 15.8 M one in the case of the $MeOH/C_6H_{12}$ mixtures. Table I also contains the second-order rate constants for the methoxymercuration of 1 in a 17.6 M $MeOH/CHCl_3$ mixture. The 18C6 concentrations—1.81 mM, 3.03 mM, 6.02 mM, and 9.03 mM—that were investigated were chosen because we wanted to carry out this study in a range where $[Hg(OAc)_2] \gg [18C6]$ and the amount of 18C6 present would be too low to appreciably affect the medium's polarity.

Inspection of the data in Table I reveals that the general trends reported[1] for our MeOH/p-dioxane mixtures are found to hold in these mixtures as well. Therefore, we will not discuss them in detail, again—for explanations of their origins and their implications see ref 1. However, it should be noted that in each solvent excellent identical linear plots of log k_2 vs. both σ and σ^+ are obtained.[6] The values of $-\rho$ and $-\rho^+$ are independent of both the solvent composition and the identity of the cosolvent. The average values of $-\rho$[7] for each solvent system are as follows: 3.18 ± 0.08, MeOH;[1] 3.29 ± 0.02, MeOH/p-dioxane;[1] 3.29 ± 0.05, $MeOH/CCl_4$; 3.10 ± 0.08, $MeOH/C_6H_{12}$; and 3.45 ± 0.10, $MeOH/CHCl_3$.

Inspection of the data in Table II shows that the values of k_2 vary with the substituent. Excellent linear plots of log k_2 vs. both σ and σ^+ are obtained.[6] The value of $-\rho$[7] for each solution is as follows: 3.07 ± 0.08, 1.81 mM; 3.02 ± 0.08, 3.03 mM; 2.91 ± 0.07, 6.02 mM; and 2.81 ± 0.06, 9.03 mM. While these values show a slight decrease as the 18C6 concentration increases, we do not believe that the trend is real since we found that after a few days, a very small amount of a fine white crystalline material[8] precipitated out of both the 6.02 and 9.03 mM 18C6 solutions. Since the composition of the kinetic mixture apparently changed somewhat with time, the values of k_2 for the less reactive members of the series are less reliable than the other ones at these 18C6 concentrations.

When the data for p-methoxystyrene are omitted, excellent identical linear plots of log k_2 vs. log [MeOH] for each styrene are obtained for both the $MeOH/CCl_4$ and the $MeOH/C_6H_{12}$ mixtures. The average values of the slopes of the correlation lines are 3.32 ± 0.29 and 3.28 ± 0.34, respectively. The corresponding value obtained for the MeOH/p-dioxane mixtures[1] is 8.98 ± 0.35. If our suggestion[1] that these values represent the number of methanol molecules required in the solvation shell during the activation process is correct, then a larger number of methanol molecules is required in the MeOH/p-dioxane mixtures than in the $MeOH/CCl_4$ and the $MeOH/C_6H_{12}$ mixtures.

Further examination of the data in Table II reveals that the values of k_2 decrease as the 18C6 concentration increases. Analyses of the data show that, while k_2 is not a linear function of [18C6], plots of log k_2 vs. log [18C6] are linear. In contrast to the results obtained in the presence of p-dioxane and CCl_4—where the values of the slopes of the log k_2 vs. log [cosolvent] correlation lines (−2.5 ± 0.1 and −1.2 ± 0.1, respectively) are independent of the substituent—the slopes of the correlation lines vary with the substituent and are fractional. The values range from −0.56 for p-methoxystyrene to −0.15 for p-nitrostyrene. These results show that the addition of 18C6 to the kinetic mixture has a smaller rate-retarding effect than the addition of one of the cosolvents does. Thus it appears that complexation of the Hg^{2+} ions by 18C6, hence p-dioxane, has a smaller effect on the rates of reaction than decreasing the solvating ability of the solvent does.

According to various theoretical equations,[9] the rate of a reaction is a function of the dielectric constant of the reaction medium. Therefore the relative reactivity of a compound in two different solvents of the same dielectric constant should be unity. If this is not the case, then some additional specific solvent effect(s) must be operative in one of the solvents but not in the other. The changes in the values of k_2 that occur upon adding CCl_4, C_6H_{12}, or $CHCl_3$ to the kinetic mixture must arise from changes in the polarity of the media. Thus the values of k_2 in mixtures of these substances should be related to the dielectric constant of the cosolvent. In order to test these ideas, we compared the values of k_2 for each styrene in $MeOH/CCl_4$ with those in $MeOH/C_6H_{12}$ and $MeOH/CHCl_3$ mixtures of the same MeOH concentration.

The dielectric constants of CCl_4, C_6H_{12}, and $CHCl_3$ are 2.23, 2.01, and 4.72, respectively. Accordingly, in methanolic mixtures of the same MeOH concentration, the values of k_2 for a given styrene in $MeOH/CCl_4$ and $MeOH/C_6H_{12}$ mixtures should be essentially the same, while those in the corresponding $MeOH/CHCl_3$ and $MeOH/CCl_4$ mixtures should be different. Inspection of the data in Table I shows, in almost all cases, that these expectations are fulfilled. The average relative reactivities—$k_2(MeOH/CCl_4)/k_2(MeOH/C_6H_{12})$ = 1.1 ± 0.1 and $k_2(MeOH/CHCl_3)/k_2(MeOH/CCl_4)$ = 1.6 ± 0.2—are, with minor exceptions, independent of the MeOH concentration and the substituent. These findings show that the values of k_2 are a function of the dielectric constant of the cosolvent and are independent of the identity of the cosolvents, as long as they interact with the species present in solution in the same way.

As mentioned previously, the values of k_2 for a given styrene in MeOH/p-dioxane and in $MeOH/CCl_4$ mixtures of the same MeOH concentration are not expected to be the same. Inspection of the data in Table I shows that the values of k_2 in the $MeOH/CCl_4$ mixtures are much larger than those in the corresponding MeOH/p-dioxane mix-

---

[5] Lewis, A.; Azoro, J. *J. Org. Chem.* **1981**, *46*, 1764.

[6] The data for p-methoxystyrene showed their usual deviations from the correlation lines (see ref 5). Thus they were not included in any of the analyses involving the use of σ or σ^+.

[7] As usual and for the same reasons (see ref 11), the plots obtained by using σ-values were better than those obtained by using σ^+-values. Thus while the values of $-\rho^+$ show the same trend, they are being omitted.

[8] We are currently attempting to isolate and identify this material.

[9] (a) Kirkword, J. G. *J. Chem. Phys.* **1934**, *2*, 351. (b) Laidler, K. J.; Eyring, H. *Ann. N.Y. Acad. Sci.* **1940**, *39*, 303. (c) Abraham, M. H. *Prog. Phys. Org. Chem.* **1974**, *11*, 1.

tures. The average relative reactivities, $k_2(\mathrm{MeOH/CCl_4})/k_2(\mathrm{MeOH}/p\text{-dioxane})$, are as follows: 4.0 ± 0.4, 21.1 M mixtures; 8.7 ± 0.8, 17.6 M mixtures; and 13 ± 2, 15.8 M mixtures. These data clearly show that an effect other than the polarity of the medium is also important in the MeOH/*p*-dioxane mixtures. The fact that this effect is concentration dependent is consistent with our belief that a complex between *p*-dioxane and $Hg(OAc)_2$ is reversibly formed, eq 1.

$$\mathrm{Hg(OAc)_2 + C_4H_8O_2 \rightleftharpoons Hg(C_4H_8O_2)^{2+} + 2\,{}^{-}OAc}\ \text{(fast)} \qquad (1)$$

The first step in the mechanism for this reaction is thought[1,10] to involve the formation of an $HgOAc^+\ {}^-OAc$ ion pair (eq 2), which reacts with the styrene in the rate-determining step (eq 3). In the presence of *p*-dioxane (and 18C6), as a result of the establishment of the equilibrium given in eq 1, an additional reactive Hg^{2+} species, the complex, exists in solution. Since both the complex and the ion pair react with the styrene, the specific rate constant k_2', for the disappearance of the styrene consists of the two terms given in eq 4. Since it has been shown[10f,11] that complexed Hg^{2+} ions are less electrophilic than uncomplexed ones, the complex is expected to be less reactive than the ion pair, i.e., $k_2(\text{ion pair}) > k_2(\text{complex})$. However, as *p*-dioxane's concentration increases, the complex becomes the dominant electrophilic species present in solution and the first term in eq 4 vanishes. Since CCl_4 does not form a complex with Hg^{2+} ions, the second term in eq 4 is zero. Hence, k_2' is less sensitive to CCl_4's concentration than it is to *p*-dioxane's. At a given MeOH concentration, $k_2(\mathrm{MeOH}/p\text{-dioxane})$ decreases more than $k_2(\mathrm{MeOH/CCl_4})$. Thus the values of $k_2(\mathrm{MeOH/CCl_4})/k_2(\mathrm{MeOH}/p\text{-dioxane})$ should vary as noted above.

$$\mathrm{Hg(OAc)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HgOAc^+\ {}^-OAc}\ \text{(fast)} \qquad (2)$$

$$\mathrm{{>}C{=}C{<}\ +\ HgOAc^+\ {}^-OAc} \xrightarrow{k_2} \mathrm{[{>}C{=}C{<}{\cdot}HgOAc]^+ + {}^-OAc}\ \text{(slow)} \qquad (3)$$

$$k_2' = k_2(\text{ion pair}) + k_2(\text{complex}) \qquad (4)$$

In conclusion, since 18C6's affect on the polarity of the medium is negligible and its rate-retarding effect is much smaller than CCl_4's and C_6H_{12}'s, the results of this study show that the polarity of the medium exerts a larger effect on the rates of this reaction than complexation of Hg^{2+} ion does. We believe that this is a consequence of the fact that the polarity of medium affects both the position of the ion pair equilibrium and the stabilities of the species involved in the ground and transition states in the rate-determining step of this reaction. Complexation of the Hg^{2+} ions, on the other hand, does not affect either of these variables, it leads, instead, to the production of a new less reactive electrophilic Hg^{2+} species. The results also show that *p*-dioxane does cause a reduction in the rates of reaction by the two proposed pathways: [1] it lowers the polarity of the medium and [2] it forms a weak complex with the $Hg(OAc_2)$. Since the CCl_4 and C_6H_{12} are incapable of forming a complex with $Hg(OAc)_2$, they can only affect the rates of reaction via the first pathway.

Experimental Section

Materials. The preparations and purifications of the styrenes, mercuric acetate, *p*-dioxane, and methanol used in this study were described previously.[5] The carbon tetrachloride (MCB), cyclohexane (Aldrich), and chloroform (B & A) used were analytical reagent grade materials. Each was predried over P_2O_5 and then twice distilled from P_2O_5 (2%, w/v). The fraction distilling at 76.6 °C, 80.6 °C, and 60.6 °C, respectively, was collected in each case. These materials were used immediately. 18-Crown-6 (Gold Label, 99.5+ %) was obtained from Aldrich. It was used without further purification. Prior to use, it was stored in a dessicator over $CaCl_2$.

Kinetic Procedure. The rates of reaction were determined as previously described.[5]

Registry No. $Hg(OAc)_2$, 1600-27-7; 18-crown-6, 17455-13-9; $p\text{-MeOC}_6H_4CH{=}CH_2$, 637-69-4; $p\text{-MeC}_6H_4CH{=}CH_2$, 622-97-9; $C_6H_5CH{=}CH_2$, 100-42-5; $p\text{-FC}_6H_4CH{=}CH_2$, 405-99-2; $p\text{-BrC}_6H_4CH{=}CH_2$, 2039-82-9; $p\text{-CNC}_6H_4CH{=}CH_2$, 3435-51-6; $p\text{-NO}_2C_6H_4CH{=}CH_2$, 100-13-0.

---

(10) (a) Chatt, J. *Chem. Rev.* **1951**, *48*, 7. (b) Matteson, D. S. *Organometallic Reaction Mechanisms of the Nontransition Elements*; Academic Press: New York: 1974; Chapter 5. (c) Kitching, W. *Organometallic Reaction*; Becker, E. I., Tsutsui, M., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, p 319. (d) Pasto, D. J.; Gontarz, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 7480; **1971**, *93*, 6902. (e) Halpern, J.; Tinker, H. B. *Ibid.* **1967**, *89*, 6427.

(11) (a) Allen, E. R.; Cartlidge, J.; Taylor, M. M.; Tipper, C. F. H. *J. Phys. Chem.* **1959**, *63*, 1437, 1442. (b) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 2783.