A Linear Free Energy Study of the Ozonolysis of Ring-Substituted α-Methylstyrenes

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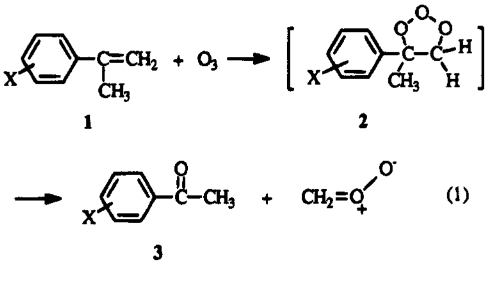
The use of linear free energy relationships to study the ozonolysis reaction has been described for a number of systems[1–3] including a series of *para*- and *meta*-substituted styrenes.[4] As part of a continuing program on the chemical bleaching of wood pulps,[5] we became interested in the effect of ring substituents on the rates of ozonolysis of some α-methylstyrenes.

The ozonolyses of substituted α-methylstyrenes (**1**) were carried out in hexane at 25 °C (eq 1). Relative reaction rates were determined by conducting ozonolyses of equimolar pairs of the substrates, i.e., pairs containing one of the substituted compounds along with unsubstituted α-methylstyrene. Ozonolysis was continued to ca. 10% conversion. The relative rates were first determined by measuring acetophenone (**3**) product ratios using quantitative capillary GLC. The results are summarized in Table 1. The relative rate data were then treated with the Hammett[6] relationship. When all data points are included, a linear plot (Figure 1) is obtained with $\varrho = -0.529$ ($R = 0.917$). If the point for *p*-methoxy is deleted, then the plot gives $\varrho = -0.552$ ($R = 0.976$). We have also treated the data with the Brown–Okamoto substituent constants. Here again, a linear plot is obtained with $\varrho^+ = -0.399$ ($R = 0.959$). In this case, the point for *p*-methoxy was included.



X = *p*-OCH$_3$, *p*-CH$_3$, *p*-Bu^t, *p*-Cl, *m*-Cl, *p*-F, *p*-NO$_2$

Obtaining relative ozonolysis rate data by following the rate of acetophenone product formation assumes that the direction of cleavage of the intermediate trioxolane (**2**) is independent of the substituent in the styrene. We have measured the direction of cleavage for some styrenes and found little dependence on the nature of the substituent.

Table 1. Relative Reactivities of Substituted α-Methylstyrenes toward Ozonolysis at 25 °C

substituent	σ^a	σ^{+a}	k_X/k_H
p-OCH$_3$	−0.28	−0.78	1.90 ± 0.08
p-CH$_3$	−0.16	−0.31	1.18 ± 0.02
p-Bu^t	−0.20	−0.26	1.35 ± 0.05
p-Cl	0.22	0.11	0.72 ± 0.02
m-Cl	0.37	0.40	0.65 ± 0.03
p-F	0.06	−0.07	0.87 ± 0.03
p-NO$_2$	0.78	0.79	0.47 ± 0.02

[a] Values taken from ref 11.

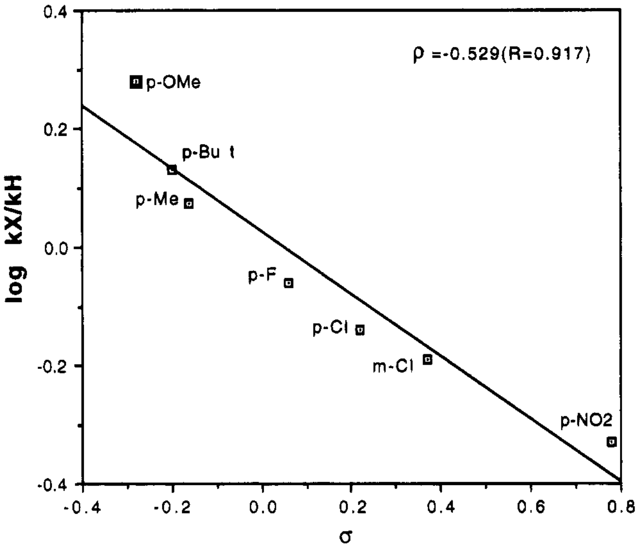


Figure 1. Plot of relative reaction rates of substituted α-methylstyrenes with ozone vs Hammett substituent constants.

Nevertheless, we have also followed the kinetics by measuring the relative rate of consumption of the styrenes. In this case, the best correlation is obtained when the *p*-methoxy and *p*-nitro substituents are excluded. This plot gives $\varrho = -0.829$ ($R = 0.955$). This value is to be compared to that found[4] ($\varrho = -0.91$) when consumption of ozone is used to obtain the rate data. As mentioned above, the ϱ value obtained (−0.529) when product appearance is used to obtain the data is subject to other influences not related to either ozone or styrene consumption and is not directly comparable to the values obtained in those studies. It is, nevertheless, a further indication of an overall electrophilic process. The plot using σ^+ constants gives $\varrho^+ = -0.469$ ($R = 0.886$) when all of the substituents are included.

The negative ϱ and ϱ^+ values obtained in these plots, using both methods of measuring the kinetics, indicate that the ozonolyses are proceeding in an electrophilic manner. This is consistent with the general observations on the ozonolysis reaction[7] and, in particular, the ozonolysis of ring-substituted styrenes.[4] When σ substituent constants are used, the correlation coefficient is improved when the *p*-methoxy compound is excluded from the plot. A comparison of the plots using σ or σ^+ substituent constants, and all the data points, indicates that the latter plot has a better correlation coefficient (0.959 vs 0.917) when acetophenone formation is the method used. This may indicate some generation of positive charge at

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the α carbon in the activated complex. Comparison of the results obtained here using styrene consumption with those found in the earlier work[4] on styrene reveals that substituent influence in the α-methylstyrene series is slightly less than in the parent styrene compounds, i.e., a smaller ϱ value is obtained. Presumably, the inductive effect of the α-methyl group reduces the influence of the ring substituents somewhat in the activated complex in the ozonolysis of the α-methylstyrenes. It is interesting to note that an earlier linear free energy study,[8] using a similar series of compounds as used here, gave somewhat comparable results. In that work, ring-substituted α-methylstyrenes were reacted with thiyl radicals at 70 °C. Treatment of the data with Hammett substituent constants gave $\varrho = -0.57$. The authors also used σ^+ constants and found an improved correlation coefficient as was observed in our work. One of their interpretations of this observation was that there may be initial complex formation between the thiyl radical and the olefin, a possibilty that cannot be ruled out in the current work.

Experimental Section

Materials. Hexane (Fisher) was distilled over calcium hydride before use. The following were used as received: α-methylstyrene (Aldrich, stabilized), *p*-chloro-α-methylstyrene (Aldrich), and *p*-fluoro-α-methylstyrene (Lancaster). The other substituted α-methylstyrenes were synthesized following literature[9] methods using methyl Grignard reagent and the appropriate aryl methyl ketone or ester. *p*-Nitro-α-methylstyrene was prepared from *p*-nitrocumene by NBS bromination followed by dehydrobromination according to a literature[10] method. The purity of all compounds used was >98% by GLC analysis. The physical properties of all prepared compounds agreed with the literature values. Sodium thiosulfate solution (N/10) was purchased from Fisher. The starch indicator was freshly prepared.

Instrumentation. Analytical GLC was carried out on a capillary gas chromatograph using a fused silica capillary column (30 m × 0.311 mm) with DB-210 as liquid phase (film thickness 0.5 μm): temperature 1, 40 °C; time 1, 5 min; rate 1, 10°/min; temperature 2, 100 °C; time 2, 2 min; rate 2, 20°/min; temperature 3, 200 °C; time 3, 5 min. Ozone was produced in a laboratory ozonator with the ozone concentration being determined using iodometry.

Ozonolyses and Kinetics. Equimolar (1.692 mmol) mixtures of the reaction pairs of unsubstituted and substituted α-methylstyrenes were weighed and then dissolved in hexane (6 mL). A reaction vessel containing the mixture was equipped with a dry ice/acetone condenser and placed in a water bath at 25 °C for 15 min prior to commencing ozonolysis. Ozone was passed into the inlet of the reaction tube. The outlet of the reaction tube was connected to a gas wash bottle containing 100 mL of 5% KI solution. Total ozone absorbed was obtained by subtracting the amount of ozone passed into the gas wash bottle from the total ozone delivered to the reaction vessel. Ozonolysis was continued to 10% conversion of the reactants (3 min, 0.167 mmol/min). The acetophenone products were identified by comparing their properties with those of the authentic materials. Quantitative determination of the products was accomplished by GLC using decane as internal standard and determining response factors for the products. When the relative rate of consumption of the styrenes was used to follow the kinetics, a similar procedure was followed involving the response factors of the styrenes. Each determination was repeated three times with excellent reproducibility.

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