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QUANTITATIVE REACTIVITY CORRELATIONS OF RING-SUBSTITUTED BENZYLMERCURIC CHLORIDE OZONOLYSIS

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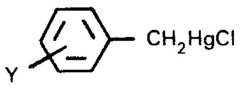
Abstract

In a Hammett study, a number of m- *and* p- *substituted benzylmercuric chlorides were allowed to compete in ozonation with benzylmercuric chloride. A linear correlation of Okamoto and Brown's* σ^+ *values gave a* ρ *value of -0.378. The result supports a five-membered cyclic transition state between benzylmercuric chloride and its derivatives with* O_3 *in which a small partial positive charge is developed at carbon.*

It has been established that organomercurials are involved in electrophilic substitution reaction[1]. Since the mercury atom shows more electropositive character than carbon, these compounds would be expected to be espectially susceptible to electrophilic substitution at carbon. Some of the well-studied cleavage of the carbon-mercury bond by protic acids, halogen, and mercuric salts have been shown to involve electrophilic mechanisms. The classical reference for ozonation of organomercurials is by Bockemuller and Pfeuffer.[2] More recent studies by Waters *et al.* on the relative rates of alkylmercuric halides[3,4] and dialkylmercurials ozonolysis indicated that electronic effects were considered to be the major factor on the reactivity order. He suggested that the mechanism of C-Hg cleavage by O_3 be depicted as a mixture of pure S_E2 and four-center processes. A high energy transition state was expected to approximate a five-membered cyclic species with a build-up of partial positive charge on carbon. If such a cyclic transition state is indeed involved, then insertion by ozone should show a correlation between the relative rate constants for the ozonation of ring-substituted benzylmercuric halides ($Y\text{-}C_6H_4CH_2HgX$) and the Hammett substituent constants (σ) of the Y-substituents.

The benzylmercuric chloride and six ring-substituted derivatives (I_{a-f}) were prepared using the grignard method as outlined by C.S. Marvel *et al.*[5] Exact structure identification of the compounds was facilitated by correlation of n.m.r. obtained $^{199}Hg\text{-}^{1}H$ spin-spin coupling data[6-8].



I_{a-f}

Y = H (a) p-CH_3O (b) p-CH_3 (c) m-CH_3
(d) p-Cl (e) m-Cl (f) m-F

In the relative rate studies, the chloroform saturated ozone solutions of approximately 7 × 10^{-3} M were allowed to react with 10^{-4} - 10^{-5} M concentrations of ring-substituted benzylmercuric chlorides. The ozone was produced by an Airox C2P-9C electric discharge ozonator. A saturated solution of ozone was prepared at 0°C, to which the solution of the organomercurial was added with stirring. To follow the course of the reaction, aliquots of 5 ml were taken and the excess ozone subsequently quenched. The change in concentration of organomercurial as a function of time was measured spectrophotometically with an UV Carey-15 Spectrophotometer equipped with a thermostated cell holder. The λ_{max}'s of the organomercurials were observed at wavelength between 245-255 nm, with molar absorptivity of 14,000-19,000 $M^{-1}cm.^{-1}$

The rate of ozonation of six-substituted benzylmercuric chlorides were determined under first order condition at 0°C in chloroform. These compounds showed a definite substituent effect on the reaction rates. Plot of the natural logarithms of organomercurial absorbances versus time yielded straight line (Figure 1), proving that the reaction is first

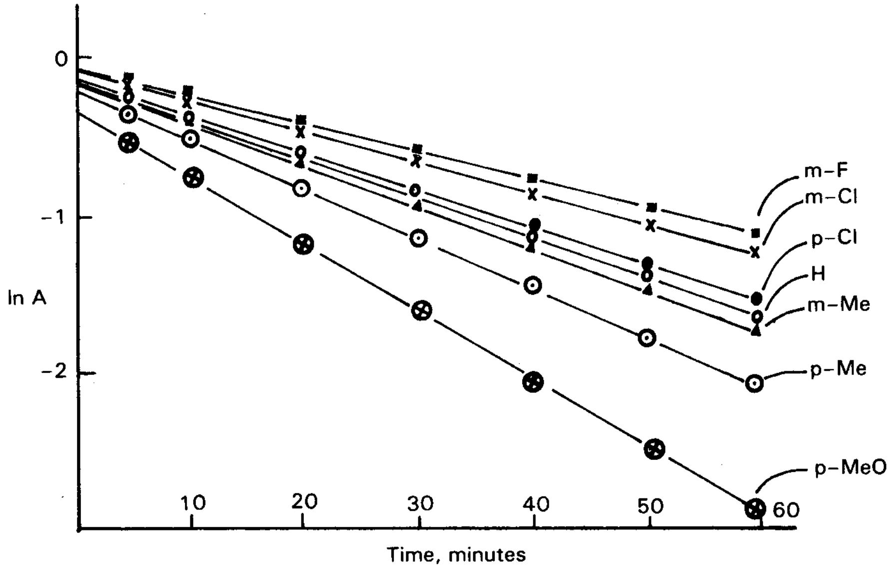


Figure 1. Plots of ln BzHgCl absorbance vs. time for pseudo first-order conditions.

TABLE 1. OZONOLYSIS RATES OF SUBSTITUTED BENZYLMERCURIC CHLORIDES[a]

Substituent X	$10^4 k'$ (sec^{-1})	k^b ($l\text{-}mole^{-1}\ sec^{-1}$)	Relative Rate[c]	Correlation Coefficient
p-CH_3O	7.050	0.097	1.95	0.9902
p-CH_3	4.767	0.066	1.33	0.9999
m-CH_3	3.686	0.052	1.05	0.9999
H	3.575	0.049	1.00	0.9999
p-Cl	3.182	0.045	0.90	0.9991
m-Cl	2.535	0.036	0.72	0.9994
m-F	2.514	0.035	0.71	0.9998

[a] Rate constants for the reaction in chloroform at 0°C.

[b] Based on O_3 concentration of the saturated solutions in each run.

[c] Based on the rate for benzylmercuric chloride 1.0000.

order in BzHgCl. Least square slope calculations of the data using a Wang 600 Programmable Calculator gave the pseudo first-order rate constants, k'. The results are summarized in Table 1, along with the relative rate of each reaction compared to benzylmercuric chloride. The correlations between log $k_{relative}$ and the Hammett σ and σ^+ constants were examined. A plot of log k_{rel} versus σ gave a poor correlation (r = 0.9494), and a ρ value of -0.581. However, a good linear correlation was found between the log k_{rel} and the Okamoto-Brown σ^+ constant (r = 0.9991) and yielded a ρ value of -0.378, as shown in Figure 2 and 3.

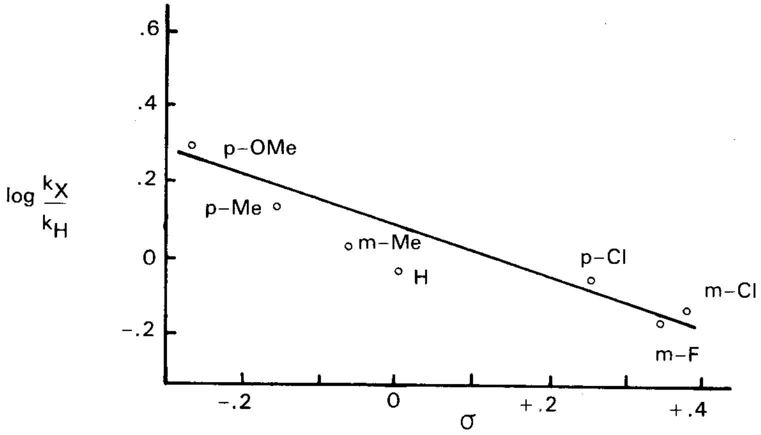


Figure 2. Plots of Hammett σ values vs. log relative rate constants

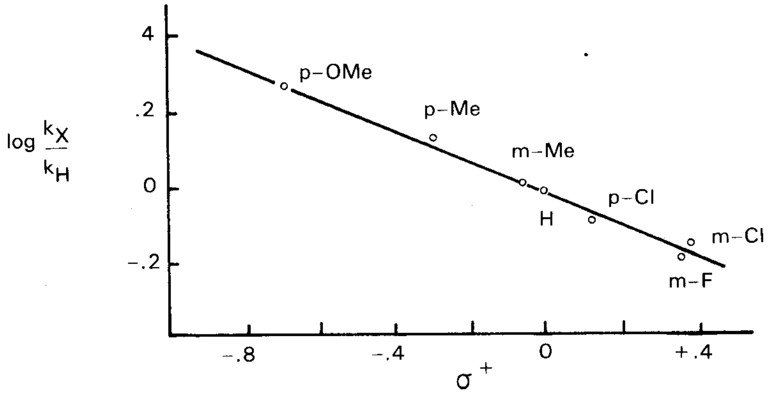


Figure 3. Plots of Okamoto-Brown σ^+ values vs. log relative rate constants

Quantitatively, the satisfactory agreement of the Hammett equation with the experimental rate constant values indicates, that electron releasing substituents favor ozone attack on the C-Hg bond. The small ρ values of - 0.378 is not uncommon for concerted process[9,10] in which a small partial positive charge is developed at the carbon to which the aryl is attached in the cyclic transition state.

Acknowledgements

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บทคัดย่อ

ปฏิกิริยาเปรียบเทียบระหว่างเบนซิลเมอร์คูริคคลอไรด์และอนุพันธ์กับโอโซนได้ศึกษาด้วยวิธี Hammett ผลความสัมพันธ์เชิงลีเนียร์แบบ Okamoto–Brown's σ^+ ให้ ρ มีค่า –0.378 ซึ่งสนับสนุนรูปสถานะเปลี่ยนแปลงเป็นวงขนาดห้าเหลี่ยมโดยที่อะตอมของคาร์บอนมีความเป็นบวกของประจุเพิ่มขึ้นเล็กน้อย