

A HAMMETT CORRELATION FOR THE ADDITION OF ORGANOTIN HYDRIDE TO BENZALDEHYDES

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(Received August 2nd, 1971)

SUMMARY

The relative rates for tri-n-butyltin hydride additions to substituted benzaldehydes under free radical and polar conditions have been determined from competitive reactions. The relative rates have been correlated by the Hammett σ or σ^+ constants. The polar addition is correlated best by σ and the free radical addition by σ^+ . Interpretations of the results are presented.

INTRODUCTION

Organotin hydrides will add to aldehydes and ketones to form stannyl alkoxides, eqn. (1)¹. This reaction is particularly interesting because addition may proceed either by a free radical or by a polar mechanism. The free radical addition may



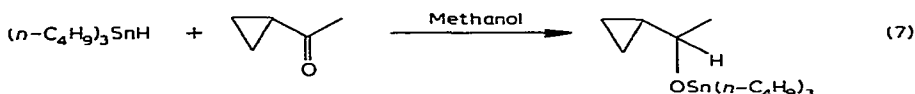
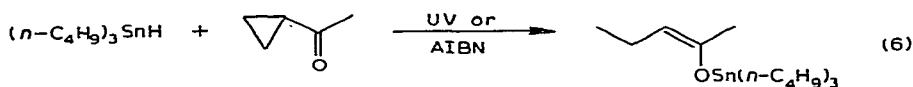
be represented as a chain process with the propagation steps shown in eqns. (2) and (3). Little is known about the details of the polar addition². If an analogy can be



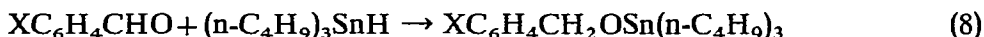
made with the polar addition to the carbon-carbon double bond, the mechanism might be represented as shown in eqns. (4) and (5)^{3,1b}.



In most cases, the addition products from the two pathways are identical, however it has recently been shown that different products may arise from the two pathways. For example, free radical addition of tri-n-butyltin hydride to cyclopropyl methyl ketone initiated by light or azobisisobutyronitrile (AIBN) results in ring opening, eqn. (6), whereas the polar addition in methanol gives the usual 1, 2 addition product, eqn. (7)⁴.



In connection with their study on the reaction of organotin hydrides and acyl halides, Kuivila and Walsh correlated the free radical addition of tri-*n*-butyltin hydride to substituted benzaldehydes with Hammett's σ values⁵. They also measured the relative rates of the polar addition to three benzaldehydes catalyzed by tri-*n*-butyltin chloride. We were interested in examining further, polar effects on the addition of organotin hydrides to aromatic aldehydes and testing the results by the Hammett relationship. In this reaction one has the opportunity to compare the substituent effects on one reaction proceeding through different mechanisms. The systems studied included the addition of tri-*n*-butyltin hydride to substituted benzaldehydes, eqn. (8), (I), catalyzed by zinc chloride at 25°; (II), initiated by azobisisobutyronitrile at 65°; (III), catalyzed by methanol at 65°; and (IV) uncatalyzed thermal addition at 110°.



RESULTS AND DISCUSSION

The experiments were carried out by allowing a mixture of benzaldehyde and a substituted benzaldehyde to compete for an insufficient amount of tri-*n*-butyltin hydride. Relative rates were calculated by the Ingold-Shaw equation⁶, where $[c_x]_i$ and $[c_x]_f$ represent the initial and final concentrations of substituted benzaldehyde and $[c_o]_i$ and $[c_o]_f$ represent the initial and final concentrations of benzaldehyde.

TABLE I

RELATIVE REACTIVITIES OF ALDEHYDES XC_6H_4CHO IN ALKOXIDE FORMATION

X	Series				Ref. 5 ^c
	(I) ^a	(II) ^b	(III) ^c	(IV) ^d	
<i>p</i> -CH ₃	0.30 ± 0.02	0.43 ± 0.05	0.46 ± 0.02	0.59 ± 0.05	1.18 ± 0.01
<i>p</i> -OCH ₃	0.33 ± 0.04	0.13 ± 0.03	0.39 ± 0.05	0.14 ± 0.06	< 0.16
<i>m</i> -CH ₃	0.44 ± 0.05	0.66 ± 0.08	0.71 ± 0.04	0.80 ± 0.07	1.03 ± 0.03
H	1.00	1.00	1.00	1.00	1.00
<i>m</i> -OCH ₃	1.07 ± 0.10	0.87 ± 0.12	1.80 ± 0.09	0.84 ± 0.18	
<i>p</i> -Cl	8.13 ± 0.37	2.65 ± 0.12	2.34 ± 0.19	1.90 ± 0.08	1.93 ± 0.06
<i>m</i> -F				3.09 ± 0.11	
<i>m</i> -Cl		4.34 ± 0.22	7.67 ± 0.37		5.42 ± 0.42

^a System: 1 g XC_6H_4CHO /1 g C_6H_5CHO /1 g diglyme/3 g $(n-C_4H_9)_3SnH$ /1.4 g anhydrous zinc chloride, at 25°. ^b System: 1 g XC_6H_4CHO /1 g C_6H_5CHO /1 g diglyme/3 g $(n-C_4H_9)_3SnH$ /0.04 g AIBN (azobisisobutyronitrile), at 65°. ^c System: 1 g XC_6H_4CHO /1 g C_6H_5CHO /1 g diglyme/anhydrous methanol (added to a volume of 10 ml)/3 g $(n-C_4H_9)_3SnH$, at 65°. ^d System: 1 g XC_6H_4CHO /1 g C_6H_5CHO /1 g diglyme/3 g $(n-C_4H_9)_3SnH$, at 110°. ^e In 2,3-dimethylbutane, (0.63 M) at 25°.

$$\frac{k_x}{k_0} = \log \frac{[c_x]_i/[c_x]_f}{[c_0]_i/[c_0]_f}$$

It can be seen from the results shown in Table 1 that electron withdrawing groups increase the rate of organotin hydride addition with respect to benzaldehyde for each series. Results for the Hammett correlations are shown in Table 2. Enhancement of the relative rates by electron withdrawing groups results in a positive ρ value for each series. Plots are shown in Fig. 1 to 4.

A least squares treatment shows that the free radical additions are best correlated by σ^+ and polar additions by σ . The experiments of Kuivila and Walsh involved a free radical addition at 25°. They obtained a ρ value of +1.85 but the point for *p*-anisaldehyde was significantly below the line. If the σ^+ constants are used, a better correlation is obtained, (see Table 2). The ρ value changes from +1.85 to +1.18. The same observation was made for the free radical additions at 65° and 110°: in each case data from repeated runs with *p*-anisaldehyde deviated significantly from the line defined by the other points. However, use of the σ^+ constants resulted in a better correlation. In the case of the polar additions no correction was necessary. Since the use of the σ^+ parameter is usually associated with the development of a positive charge conjugated with the aromatic nucleus in the transition state and negative ρ values, it might seem surprising that a reaction with a positive ρ value should show a need for the σ^+ parameter. This phenomenon has previously been observed for other free radical additions to aromatic carbonyl compounds^{5,7}. Kuivila and Walsh attributed the observation to conjugation between the substituent and the carbonyl group in the ground state⁵. The conjugation lowers the energy of the

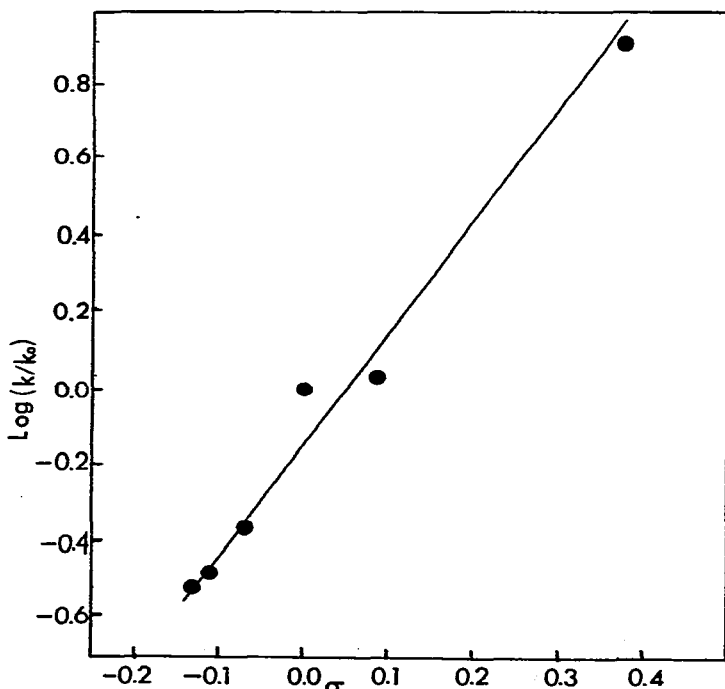


Fig. 1. Hammett plot for alkoxide formation from substituted benzaldehydes at 25°, Series (I).

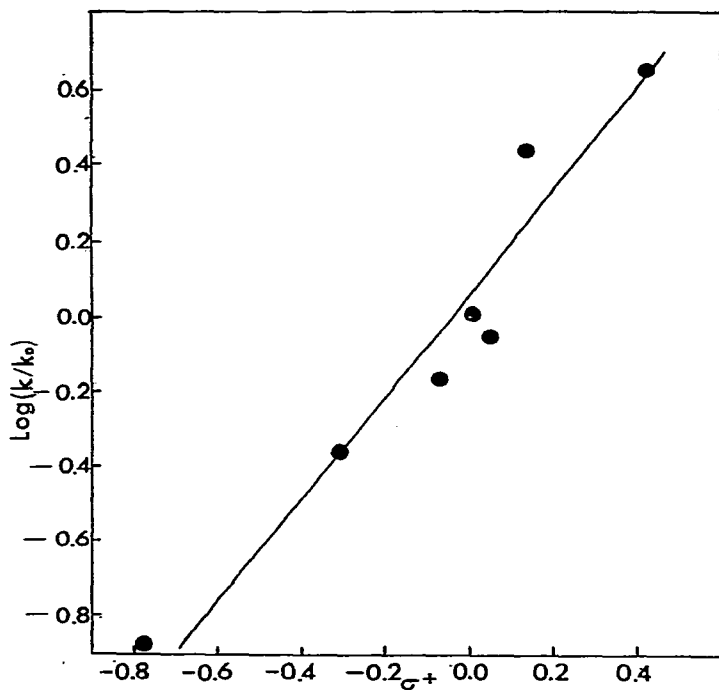


Fig. 2. Hammett plot for alkoxide formation from substituted benzaldehydes at 65°, Series (II).

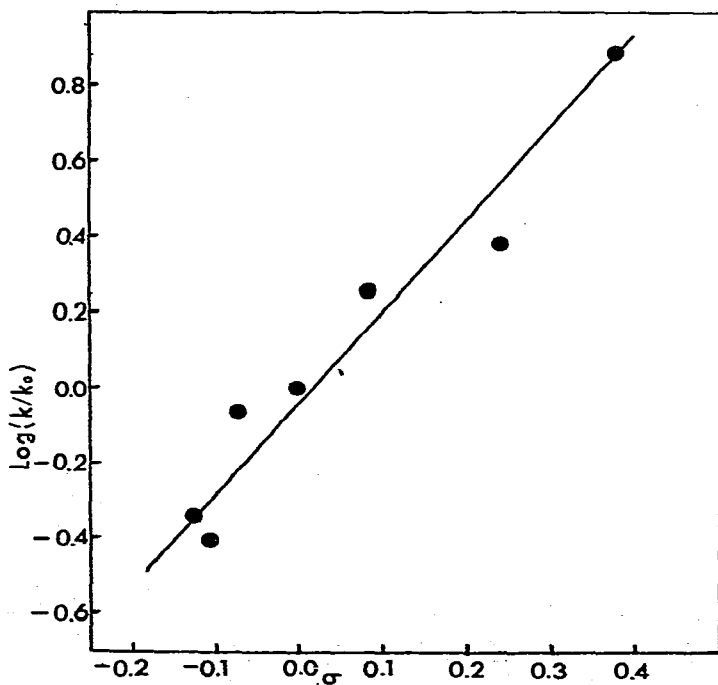


Fig. 3. Hammett plot for alkoxide formation from substituted benzaldehydes at 65°, Series (III).

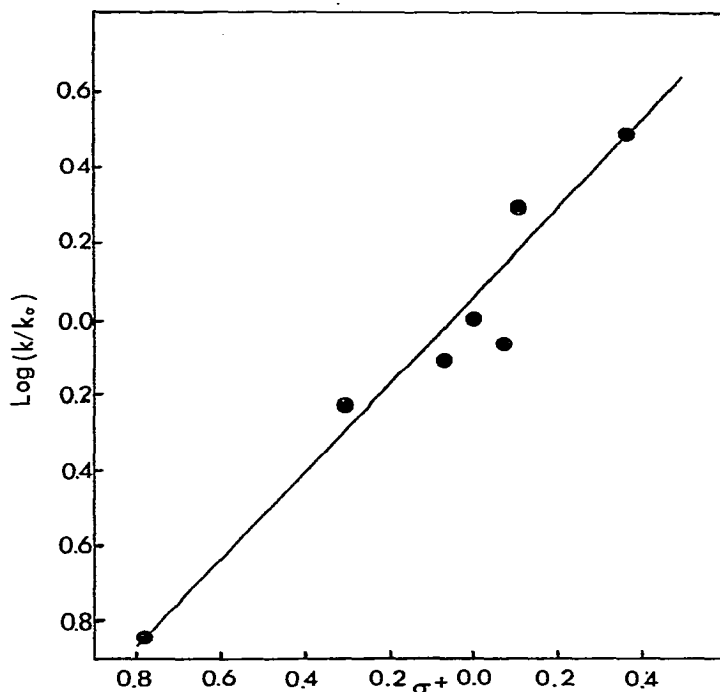


Fig. 4. Hammett plot for alkoxide formation from substituted benzaldehydes at 110°, Series (IV).

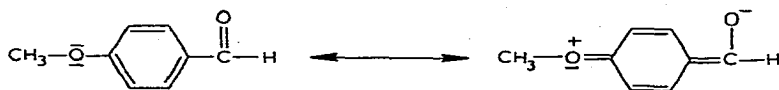
TABLE 2

RESULTS OF HAMMETT PLOTS FOR THE ADDITION OF ORGANOTIN HYDRIDES TO SUBSTITUTED BENZALDEHYDES

Series	Observed ρ value	r^a	Substituent parameter	Proposed mechanism
(I)	+3.75	0.98	σ	Polar
(I)	+1.06	0.66	σ^+	Polar
(II)	+2.42	0.91	σ	Free radical
(II)	+1.33	0.97	σ^+	Free radical
(III)	+2.33	0.97	σ	Polar
(III)	+1.07	0.88	σ^+	Polar
(IV)	+1.54	0.75	σ	Free radical
(IV)	+1.13	0.98	σ^+	Free radical
Ref. 5	+1.89	0.78	σ	Free radical
Ref. 5	+1.18	0.95	σ^+	Free radical

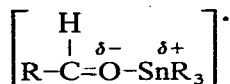
^a Least squares correlation coefficient.

ground state and this energy lowering must be overcome in passing to the transition state.



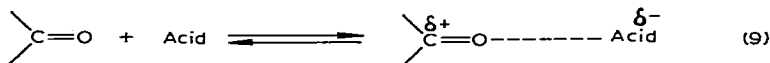
The positive ρ value for the radical additions may be understood if the tin

radical is assumed to be nucleophilic⁸, and polar factors are of consequence in the transition state⁹. Electron withdrawing groups would then help to stabilize the partial negative charge on the aromatic aldehyde.



The polar additions at 25° and 65° were both correlated well with the standard σ values. In both cases, the ρ values were more positive than those for the free radical reactions run at the same temperature. It is important to note that the σ^+ parameter has very little predictive value particularly when compared with "normal" substituent constants¹⁰. A valid means of assessing relative reactivity data is to use the normal values for *meta* substituents thereby reducing the abnormality due to conjugative interaction. At 25° the free radical addition would have a ρ value of about +2.0 using only the values for the *meta* substituents⁵, which is still less than the value, +3.75 found for the zinc chloride catalyzed reaction in this study. This finding is in contrast to the observation by Kuivila and Walsh which indicated the polar addition, catalyzed by the Lewis acid, tri-*n*-butyltin chloride, was less sensitive to polar effects than the free radical addition⁵. At 65° the ρ values are comparable, about +1.9 for the free radical addition using the *meta* values and +2.33 for the polar addition.

Neumann has suggested that the addition of organotin hydride in the presence of Lewis acids is preceded by complex formation, eqn. (9)^{1a}. The complex formation increases the electron deficiency of the carbonyl carbon thereby facilitating hydride



transfer from tin to carbon. For a rough comparison, the ρ value for hydride transfer from tin at 25° is higher than that reported for the more reactive metal hydride, sodium borohydride (ρ +2.81 at 26° in pyridine¹¹; ρ +2.6 at 0° in isopropyl alcohol¹²). If the carbonyl group is made sufficiently electron deficient, the polar addition of organotin hydride will occur without catalyst¹³. The ρ value for the zinc chloride and methanol catalyzed reactions should reflect the overall process of complex formation followed by subsequent hydride transfer. This overall process is correlated by σ . The positive ρ value for the polar addition is readily understood in view of the demonstrated ability of electron withdrawing groups to facilitate the polar hydride transfer¹³.

In conclusion, a Hammett correlation of the free radical and polar additions of tri-*n*-butyltin hydride to a series of benzaldehydes shows clearly a difference in substituent effects for the two mechanisms. While the absolute magnitudes of the ρ values are not strictly comparable due to differing reaction conditions, the use of the σ^+ substituent constants for the free radical additions and normal σ values for the polar additions demonstrates the different type of substituent interactions in the two cases.

EXPERIMENTAL

The indicated amounts of the two competing aldehydes, diglyme and solvent

were mixed in small stoppered flasks, see Table 1. The flasks were equilibrated at the temperatures indicated in Table 1. The indicated amount of tri-n-butyltin hydride was then added to the reaction flasks. Both aldehydes were in excess of the amount of hydride used [AIBN was added with the organotin hydride in series (II)]. The mixture was allowed to stand until all of the tin hydride had been consumed as indicated by the disappearance of the tin-hydrogen stretching band in the infrared spectrum. The mixture was analyzed by gas liquid partition chromatography before and after the reaction using diglyme as the internal standard. The relative rates were calculated by the equation of Ingold and Shaw, (see results and discussion section).

Analyses were carried out on a F and M Model 810 Gas Chromatograph with an eight foot, stainless steel column packed with 10% Carbowax 20M on 60-80 mesh Chromosorb P, (in the case of the methanol catalyzed reactions, the column was packed with 10% Carbowax 20M on 60-80 mesh Chromosorb G). The analyses were run isothermally at 190° with a flow rate of 80 ml/min of helium.

ACKNOWLEDGEMENT

The authors are grateful to Dr. Henry G. Kuivila for helpful discussions and suggestions during the preparation of this paper.

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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