

LINEAR FREE ENERGY RELATIONSHIPS IN A METAL ION-CATALYSED ESTERIFICATION OF SUBSTITUTED BENZOIC ACIDS WITH ETHYLENE GLYCOL*

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Rates of an uncatalysed and Pb^{2+} ion-catalysed esterification of thirteen *ortho*, *meta*- and *para*-substituted benzoic acids with ethylene glycol in excess were measured. The uncatalysed reaction was first-order and the catalysed reaction was half-order in the acid. The values of Hammett reaction constants for the uncatalysed (ρ_0) and catalysed (ρ_c) reactions of the *meta*- and *para*-substituted acids were 0.54 ± 0.07 and 0.48 ± 0.03 , respectively; they did not differ too much from the reaction constants for the acid-catalysed esterification of corresponding benzoic acids with alcohols. The *p*-methoxy derivative deviated considerably from the linear correlation owing to the "through-resonance" effect. The four-parameter Yukawa-Tsuno equation gave improved fit of the data, yielding a value of 0.48 ± 0.02 for the ρ_c' constant. The effect of *ortho* substituents upon the rate of the metal ion-catalysed esterification reaction could be best correlated by the two-parameter Taft equation; the ρ_c^* and δ_c constants equaled to 0.56 ± 0.01 and 0.62 ± 0.00 , respectively.

The kinetics and mechanism of metal ion-catalysed hydrolysis of esters, especially amino-esters in an aqueous medium continues to be a matter of great interest¹⁻³; the catalytic or promoting effect of metal ions, which in many cases was demonstrated by rate acceleration by several orders of magnitude compared to the uncatalysed reaction, was generally termed the "super-acid" catalysis, as suggested by Westheimer^{3,4}. This great catalytic effect resulting in a stabilization of transition state and thus in lowering the energy barrier was ascribed to formation of chelate complexes between a metal ion and the transition state. On the other hand, very little is known about the mechanism of the reverse reaction, *i.e.* the metal ion-catalysed esterification of carboxylic acids by mono- and polyhydric alcohols. In the previous work of this series⁵ we reported the kinetics of esterification of benzoic acid with aliphatic glycols in the presence of various compounds of Group II.—V., VII. and VIII. metals as catalysts. The activation parameters of the reaction and the dependence of reaction rate on the glycol structure were determined. This model reaction was found to be half-order both in the monocarboxylic acid and in Ti^{4+} , Sn^{2+} and Pb^{2+} ions. Titanium(IV) and tin(II) compounds were the most efficient catalysts. Although these measurements made it possible to express quantitatively the catalytic activity of metal ions and pointed to the complexity of the reaction course in comparison with the un-

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catyalsed reaction, many questions concerning the mechanism of the metal ion-catyalsed formation of esters from carboxylic acids and glycols have not been answered.

In an effort to get additional data which could elucidate the action of a metal catalyst in the esterification of aromatic carboxylic acids with glycols, we have measured the rates of both uncatalysed and metal ion-catalysed esterification of thirteen *ortho*-, *meta*- and *para*-substituted benzoic acids with ethylene glycol. The reaction rates were determined under normal pressure at 197°C and in a system that practically prevented the reversible reaction to occur. The reactions accelerated by the most efficient catalysts proceeded under such conditions at a high rate; to achieve higher accuracy of the measurements, lead(II) oxide exhibiting low activity was therefore chosen as a catalyst. The rate constants obtained were treated by linear free energy relationships.

EXPERIMENTAL

Compounds used. *Ortho*-, *meta*- and *para*-substituted benzoic acids, all reagent-grade chemicals (Fluka A. G., Buchs), were purified by crystallisation from appropriate solvents. Their purity was checked by titration⁵ and in all cases it was higher than 99.2%. *o*-Chlorobenzoic acid (acetone), m.p. 139–140°C (ref.⁶ m.p. 140.6°C); *p*-chlorobenzoic acid (aq. ethanol), m.p. 241.0 to 241.5°C (ref.⁶ m.p. 241.2°C); *o*-toluic acid (aq. ethanol), m.p. 104.9°C (ref.⁷ m.p. 106–107°C); *m*-toluic acid (water), m.p. 114.0–114.5°C (ref.⁷ m.p. 114.4–115.0°C); *p*-toluic acid (aq. ethanol), m.p. 183.0–183.5°C (ref.⁷ m.p. 183.0–183.5°C (ref.⁷ 182–183°C); *o*-methoxybenzoic acid (ethanol), m.p. 100–101°C (ref.⁸ m.p. 101.3°C); *p*-methoxybenzoic acid (water), m.p. 183.5 to 184.5°C (ref.⁹ m.p. 184.2°C); *o*-bromobenzoic acid (water), m.p. 147–148°C (ref.⁶ m.p. 148°C); *p*-bromobenzoic acid (water), m.p. 250–251°C (ref.⁶ m.p. 250.4°C); *o*-nitrobenzoic acid (water), m.p. 146–147°C (ref.⁶ m.p. 145.2°C); *m*-nitrobenzoic acid (benzene), m.p. 141.5–142°C (ref.⁶ m.p. 141.1°C); *p*-nitrobenzoic acid (n-butanol), m.p. 240–241°C (ref.⁶ m.p. 242.2°C); *m*-trifluoromethylbenzoic acid (aq. ethanol), m.p. 101.0–101.5°C (ref.¹⁰ m.p. 103.0–104.5°C). Ethylene glycol (Spolana, Neratovice) was distilled in a nitrogen atmosphere and the fraction boiling at 94°C/11 Torr was collected; it contained 0.02% of diethylene glycol and 0.2% of water. Lead(II) oxide of analytical grade purity (Lachema, Brno) contained 93.47% Pb and was used without further purification. Nitrogen (Tesla, Vrchlabi) was used as an inert gas; it contained 0.1% (v/v) of oxygen. Melting points were determined with a Kofler hot stage microscope and are uncorrected.

Analytical methods. A decrease in the concentration of substituted benzoic acids in the esterification mixture with time as well as the purity of these acids was determined by acidimetric titration; the procedure and apparatus were described in the previous work⁵.

Kinetic measurements. Esterification rate constants were determined using the apparatus and methods reported earlier⁵. The initial molar ratio of the acids to ethylene glycol was 1 : 30, the lead(II) oxide concentration was $2 \cdot 10^{-3}$ mol kg⁻¹ in all experiments. The water formed during the esterification reactions was removed immediately from the reacting system by a stream of nitrogen whose flow rate was 3.5 l/h. At this flow rate, the given amounts of reactants and at a stirring intensity of 200 rev./min, the reactions proceeded in the kinetic region. Volume changes of the reaction mixtures due to water evaporation during the reactions were less than 2% and were not included in the calculations. The transformation of the acids into the corres-

ponding esters was followed over at least two and mostly three half-times. Each reaction constant was an average of two, sometimes three or four separate measurements. The standard deviations from regression lines and the correlation coefficients are given in Table I.

Isolation of products. The 2-hydroxyethyl esters and ethylene glycol dibenzoates of the corresponding substituted benzoic acids were isolated by the previously reported procedures¹¹. Their elemental analyses, boiling points and mixed melting points with authentic samples of the products prepared by the earlier reported procedure¹¹ agreed well with the expected data.

RESULTS AND DISCUSSION

The plots of $2.303 \cdot \log [A]_0/[A]$ (A is an *ortho*-, *meta*- or *para*-substituted benzoic acid) vs time for the uncatalysed esterification reactions with ethylene glycol were straight lines for all the acids investigated. Under the conditions used and with ethylene glycol in a substantial excess over the carboxylic acid, the reactions followed

TABLE I

Rate Constants for the Uncatalysed (k_0) and Pb^{2+} Ion-Catalysed (k_c) Esterification of *ortho*-, *meta*- and *para*-Substituted (X) Benzoic Acids (A) with Ethylene Glycol (B)

$[A]_0 = 0.5043 \text{ mol kg}^{-1}$, $[B]_0 = 15.1290 \text{ mol kg}^{-1}$, $[PbO] = 2 \cdot 10^{-3} \text{ mol kg}^{-1}$; temperature $197 \pm 0.5^\circ\text{C}$.

X	σ^-	$10^3 \cdot k_0$ h^{-1}	$r(k_0)$	$10^3 \cdot k_c$ $\text{mol}^{1/2} \text{ kg}^{-1/2} \text{ h}^{-1}$	$r(k_c)$
<i>o</i> -Methyl	—	80 ± 1	0.9980	88 ± 1	0.9998
<i>o</i> -Methoxy	—	273 ± 1	0.9999	245 ± 1	0.9995
<i>o</i> -Nitro	—	92 ± 1	0.9973	104 ± 1	0.9996
<i>o</i> -Bromo	—	206 ± 2	0.9991	153 ± 1	0.9993
<i>o</i> -Chloro	—	256 ± 2	0.9993	193 ± 1	0.9995
<i>m</i> -Methyl	-0.07^a	190 ± 1	0.9996	215 ± 2	0.9994
<i>m</i> -Trifluoromethyl-		332 ± 2	0.9996	364 ± 4	0.9988
<i>m</i> -Nitro	0.69^a	432 ± 5	0.9983	490 ± 4	0.9995
<i>p</i> -Methyl	$-0.15^{a,b}$	174 ± 2	0.9976	195 ± 2	0.9993
<i>p</i> -Methoxy	-0.60^c	113 ± 1	0.9987	145 ± 1	0.9988
<i>p</i> -Nitro	$1.24^{a,d}$	507 ± 4	0.9987	520 ± 8	0.9963
<i>p</i> -Bromo	$0.25^{a,e}$	307 ± 7	0.9945	302 ± 1	0.9993
<i>p</i> -Chloro	0.22^a	280 ± 4	0.9972	290 ± 2	0.9996
Hydrogen ^f	—	230 ± 1	0.9997	255 ± 1	0.9998

^a Calculated from the ionisation constant of the corresponding substituted phenol (ref.¹²); ^b ref.¹³ -0.15 and ref.¹⁴ -0.14 ; ^c refs.¹⁵⁻¹⁷; the values calculated from the ionisation constants of *p*-methoxyphenol and *p*-anisidine correspond to -0.13 and -0.26 , respectively, in agreement with ref.¹²; ref.¹³ -0.13 and ref.¹⁶ -0.12 ; ^d ref.¹³ 1.24 , ref.¹⁴ 1.25 ; ^e ref.¹³ 0.25 , ref.¹⁶ 0.26 ; ^f the values of the rate constants were taken from the previous work⁵.

the pseudo-first order rate law and their kinetics could be described by the empirical equation (1). The values of the corresponding rate constants

$$-d[A]/dt = k_0[A] \quad (1)$$

k_0 computed from the slopes of the first-order plots and refined by the least-squares method are presented in Table I. The linear dependences of $2([A]_0^{1/2} - [A]^{1/2})$ on time confirmed in all cases the pseudo-half order kinetics for the esterification of substituted benzoic acids with ethylene glycol catalysed by lead(II) oxide. The values of the corresponding pseudo-half order constants k_c , which were determined from the slopes of the straight lines of the half-order plots in agreement with Eq. (2) and refined by the least-squares method, are listed in Table I. The pseudo-first order kinetics for the uncatalysed reaction and the pseudo-half order kinetics for the metal ion-

$$k_c = 2([A]_0^{1/2} - [A]^{1/2})/t \quad (2)$$

-catalysed reaction coincide with the rate laws found for analogous esterifications of benzoic acid with aliphatic glycols in our preceding work⁵. From comparison of the values of the rate constants listed in Table I it follows that in agreement with nucleophilic character of the esterification reaction, the electron-attracting substituents accelerate and the electron-donating substituents retard both the uncatalysed and metal ion-catalysed esterification of *meta*- and *para*-substituted benzoic acids. Both esterification reactions are therefore facilitated by low electron density at the reaction site. The observed reaction rates indicate the following order of reactivity: $p\text{-NO}_2 > m\text{-NO}_2 > m\text{-CF}_3 > p\text{-Cl} \approx o\text{-Br} > \text{H} > m\text{-CH}_3 > p\text{-CH}_3 \gg p\text{-OCH}_3$.

By plotting logarithms of pseudo-half order rate constants k_c for the Pb^{2+} ion-catalysed esterification of *meta*- and *para*-substituted benzoic acids against Hammett σ constants¹⁸, an excellent linear dependence was obtained ($r = 0.9958$), except for *p*-methoxybenzoic acid. The reaction constant ρ_c , which was calculated from the slope of the straight line by the least-squares method, had a value of 0.44 ± 0.02 and the Hammett correlation for this reaction series can be expressed by Eq. (3). The plot of logarithms of rate constants k_0 for the uncatalysed esterification of *meta*- and *para*-substituted benzoic acids against σ constants gave a satisfactory linear dependence

$$\log k_c = (0.44 \pm 0.02) \sigma - 0.59 \quad (3)$$

($r = 0.9876$), again with the exception of *p*-methoxybenzoic acid; in this case the reaction constant ρ_0 had a value of 0.46 ± 0.03 . The magnitudes of reaction constants ρ_c and ρ_0 are comparable with those reported for the acid-catalysed esterification of substituted benzoic acids with cyclohexanol ($\rho = 0.42$; ref.¹⁹) or with aliphatic alcohols (ρ changes from -0.2 to $+0.5$; ref.²⁰). The lower sensitivity to polar substiti-

tuent effects of the acid-catalysed esterification of aromatic carboxylic acids has been explained by compensation of two opposite effects: either the substituent accelerates the initial protonation of a carboxylic acid but retards the subsequent nucleophilic attack by an alcohol molecule, or it suppresses the protonation but facilitates the nucleophilic attack²¹. If we accept the assumption that the metal ion acts in the esterification reaction as a superacid catalyst, *i.e.* that it serves as a proton with magnified charge²², an analogous explanation can be applied also to the metal ion-accelerated esterification of aromatic carboxylic acids.

When *p*-methoxybenzoic acid was included in the Hammett correlation, the value of the constant ρ_c increased to 0.48 ± 0.03 ($r = 0.9881$) and that of the constant ρ_0 to 0.54 ± 0.07 ($r = 0.9655$). Considerable deviation of the point for the *p*-methoxy substituent from the regression line in the Hammett relation is apparent from the values of the correlation coefficients. Such a deviation has been frequently observed in a variety of reactions^{17,18,23,24} for +M class substituents (ref.²⁵) and recorded also in the above-mentioned acid-catalysed esterification of substituted benzoic acids with alcohols^{19,20}. It originates from mesomeric *para* interaction with the reaction site, which in our case leads to a decrease in the acidity of the carboxyl group of *p*-methoxybenzoic acid and to irregularity in the Hammett relation. To eliminate this "through-resonance" effect²⁶, Yukawa and Tsuno²⁷⁻³⁰ modified the standard Hammett equation, originally for correlating the rate constants of aromatic electrophilic substitution reactions; an analogous modification has been suggested by Leffler and Grunwald³¹ also for nucleophilic reactions and its correctness has been proved by a number of successful applications³²⁻³⁶. To correlate our pseudo-half order rate constants k_c , we have used the Yukawa-Tsuno relation in the form (4) where k_s is the rate constant for the reaction of unsubstituted benzoic acid and Y is a constant that has to be determined from the slope of the straight line

$$\log(k_c/k_s) = \rho'_c[\sigma + Y(\sigma^- - \sigma)] \quad (4)$$

in the plot of $[(1/\rho'_c) \log(k_c/k_s) - \sigma]$ vs $(\sigma^- - \sigma)$; σ^- 's are the corresponding nucleophilic substituent constants and σ 's are the standard Hammett substituent constants. The σ^- constants were calculated (Eq. (5)), with the exception of *m*-CF₃ and *p*-OCH₃ substituents, from the known ionisation constants of the respective substituted phenols according to the relation suggested by Biggs and Robinson¹² and are presented in Table I. For the *p*-OCH₃ substituent we used the σ^- value reported by Miller^{15,16};

$$\sigma^- = (9.919 - pK_a)/2.229 \quad (5)$$

m-trifluoromethylbenzoic acid has not been included in the Yukawa-Tsuno correlation owing to the unknown ionisation constant of *m*-trifluoromethylphenol. The constant Y was found to be 0.2. Although the extent of bond-making in the transition

state is reflected by the magnitude of the reaction constant ρ , the low value of the constant Y indicates that bond-making in the transition state of the metal ion-catalysed esterification reaction is somewhat more important than bond-breaking. By plotting logarithms of pseudo-half order rate constants k_c against $[\sigma + 0.2(\sigma^- - \sigma)]$, a linear dependence (Fig. 1) was obtained characterized by a correlation coefficient of 0.9905. The reaction constant ρ_c calculated by the least-squares method from the slope of the straight line had a value of 0.48 ± 0.02 and the Yukawa–Tsuno correlation could be expressed by Eq. (6). In this case the point for

$$\log k_c = (0.48 \pm 0.02)[\sigma + 0.2(\sigma^- - \sigma)] - 0.59 \quad (6)$$

the $p\text{-OCH}_3$ substituent deviates less from the regression line and the correlation coefficient attains higher value than in the Hammett correlation, even though at the expense of a small deviation of the point for the $p\text{-NO}_2$ group. It should be emphasized that this satisfactory correlation has been achieved by using Miller's σ^- constant^{15,16} for the $p\text{-OCH}_3$ group which has a high negative value of -0.60 ; the use of the σ^- constants calculated from ionisation constants of p -methoxyphenol¹² ($\sigma^- = -0.13$) or p -anisidine¹² ($\sigma^- = -0.26$) did not yield a satisfactory correla-

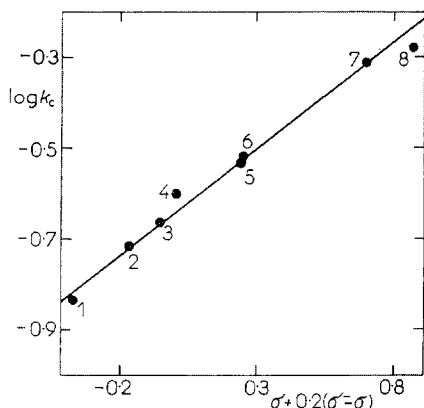


FIG. 1

A Four-Parameter Yukawa–Tsuno Correlation of Rate Constants k_c for the Lead(II) Oxide-Catalysed Esterification of *meta*- and *para*-Substituted Benzoic Acids with Ethylene Glycol

1 $p\text{-OCH}_3$, 2 $p\text{-CH}_3$, 3 $m\text{-CH}_3$, 4 H, 5 $p\text{-Cl}$, 6 $p\text{-Br}$, 7 $m\text{-NO}_2$, 8 $p\text{-NO}_2$.

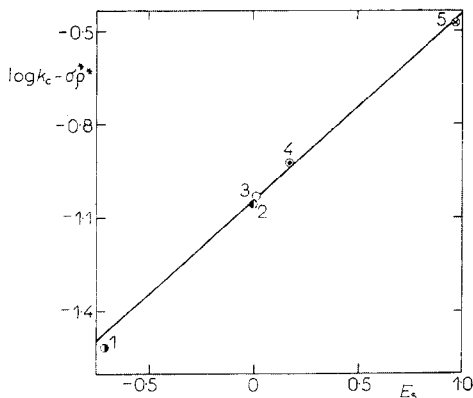


FIG. 2

A Two-Parameter Taft Correlation for the Lead(II) Oxide-Catalysed Esterification of *ortho*-Substituted Benzoic Acids with Ethylene Glycol

1 NO_2 , 2 CH_3 , 3 Br, 4 Cl, 5 OCH_3 .

tion. This fact indicates a powerful resonance requirement of the above-mentioned reaction of *p*-methoxybenzoic acid.

From Table I it becomes evident that the values of pseudo-half order rate constants k_c and pseudo-first order rate constants k_0 for the esterification of *ortho*-substituted benzoic acids decrease in the following order: $\text{OCH}_3 > \text{Cl} > \text{Br} > \text{NO}_2 > \text{CH}_3$. Attempts to correlate the logarithm of rate constants k_c with Taft³⁷⁻³⁹ polar ($\log(k_c/k_s) = \sigma^* \rho_c^*$) or steric ($\log k_c/k_s = \delta_c E_s$) substituent constants have failed; the plots of $\log k_c$ vs σ^* or E_s were quite scattered. On the other hand, an excellent linear dependence has been obtained by plotting the values of $(\log k_c - \sigma^* \rho_c^*)$ against the steric substituent constants E_s (Fig. 2), in accordance with a two-parameter Taft equation involving both polar and steric effect¹⁷. The correlation coefficient, r , which was determined by multiple regression⁴⁰ had a value of 0.9920. The reaction constants ρ_c^* and δ_c calculated from the slope of the line shown in Fig. 2 by the least-squares method equaled to 0.56 ± 0.01 and 0.62 ± 0.00 , respectively, and the Taft correlation could be expressed by Eq. (7)

$$\log k_c = (0.56 \pm 0.01) \sigma^* + (0.62 \pm 0.00) E_s - 1.06. \quad (7)$$

From confrontation of this equation with the values of rate constants k_c for the esterification of the *ortho*-substituted acids (Table I) it follows that Eq. (7) reproduces the values of $\log k_c$ with an error of 0.4–4.3% over the range of σ^* and E_s constants 1.19 and 1.68, respectively. The positive value of the reaction constant ρ_c^* shows that the electron-attracting groups accelerate and electron-donating groups retard the esterification of the *ortho*-substituted acids. As follows from the correlation expressed by Eq. (7), polar and steric effects are comparable in the Pb^{2+} ion-catalysed esterification reaction of these acids and the free energy of activation for these reactions is thus the sum of independent contributions of polar and steric effects. Resonance effects do not play a significant role in the esterification reaction of the *ortho*-substituted acids. Comparison of the reaction constant ρ_c^* for the esterification of *ortho*-substituted benzoic acids with the reaction constant ρ_c' for the esterification of *meta*- and *para*-substituted acids shows that polar effects are nearly the same in the *ortho*-, *meta*- and *para*-series of substituted benzoic acids. Identical kinetic laws found for the metal ion-catalysed esterification of benzoic acid with aliphatic glycols⁵ and of *ortho*-, *meta*- and *para*-substituted benzoic acids with ethylene glycol lead to the conclusion that linear free energy relationships established in this work hold very likely for the esterification of aromatic carboxylic acids with aliphatic glycols in general, irrespective of whether this reaction is catalysed by Pb^{2+} or other catalytically active metal ions.

REFERENCES

1. Bender M. L.: *Advan. Chem. Ser.* 37, 19 (1963).
2. Jones M. M., Connor W. A.: *Ind. Eng. Chem.* 55, 15 (1963).
3. Bender M. L.: *Mechanism of Homogeneous Catalysis from Protons to Proteins*, p. 211. Wiley-Interscience, New York 1971.
4. Westheimer F.: *Trans. N. Y. Acad. Sci.* 18, 15 (1955).
5. Habib O. M. O., Málek J.: *This Journal* 41, 2724 (1976).
6. Norris J. F., Strain W. H.: *J. Amer. Chem. Soc.* 57, 187 (1935).
7. Smith H. A., Stainfield J. A.: *J. Amer. Chem. Soc.* 71, 81 (1949).
8. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Vol. 1, p. 330. Elsevier, Amsterdam 1950.
9. Hodgman Ch. D.: *Tables for Identification of Organic Compounds*, p. 127. Chemical Rubber Publishing Co., Cleveland 1960.
10. Roberts J. D., Curtin D. Y.: *J. Amer. Chem. Soc.* 68, 1658 (1946).
11. Habib O. M. O., Málek J.: *This Journal* 41, 2543 (1976).
12. Biggs A. I., Robinson R. A.: *J. Chem. Soc.* 1961, 388.
13. Cohen L. A., Jones W. M.: *J. Amer. Chem. Soc.* 85, 3397 (1963).
14. Fischer A., Leary G. J., Topson R. D., Vaughan J.: *J. Chem. Soc. (B)* 1966, 782.
15. Miller J.: *Aust. J. Chem.* 9, 61 (1956).
16. Miller J.: *J. Amer. Chem. Soc.* 79, 93 (1957).
17. Wells P. R.: *Chem. Rev.* 63, 171 (1963).
18. Jaffé H. H.: *Chem. Rev.* 53, 191 (1953).
19. Hartman R. J., Hoogsteen H. M., Moede J. A.: *J. Amer. Chem. Soc.* 66, 1714 (1944).
20. Chapman N. B., Shorter J.: *Advances in Linear-Free Energy Relationships*, p. 74. Plenum Press, London 1972.
21. Ingold C. K.: *Structure and Mechanism in Organic Chemistry*, Chapter 15. Cornell University Press, Ithaca, New York 1969.
22. Ref.³, p. 212.
23. Van Bekkum H., Verkade P. E., Wepster B. M.: *Rec. Trav. Chim. Pays-Bas* 78, 815 (1959).
24. Exner O.: *This Journal* 31, 65 (1966).
25. Hammett L. P.: *Physical Organic Chemistry*, 2. Ed., p. 359. McGraw-Hill, New York 1970.
26. Clark J., Perrin D. D.: *Quart. Rev. (Chem. Soc.)* 18, 295 (1964).
27. Tsuno Y., Isabata T., Yukawa Y.: *Bull. Chem. Soc. Jap.* 32, 960 (1959).
28. Tsuno Y., Yukawa Y.: *Bull. Chem. Soc. Jap.* 32, 965 (1959).
29. Tsuno Y., Yukawa Y.: *Bull. Chem. Soc. Jap.* 32, 971 (1959).
30. Yukawa Y., Tsuno Y., Sawada M.: *Bull. Chem. Soc. Jap.* 39, 2274 (1966).
31. Leffler J. E., Grunwald E.: *Rates and Equilibria of Organic Reactions*, p. 214. Wiley, New York 1963.
32. Ryan J. J., Humffray A. A.: *J. Chem. Soc. (B)* 1966, 842.
33. Humffray A. A., Ryan J. J.: *J. Chem. Soc. (B)* 1967, 468.
34. Ryan J. J., Humffray A. A.: *J. Chem. Soc. (B)* 1967, 1300.
35. Yukawa Y., Tsuno Y., Sawada M.: *Bull. Chem. Soc. Jap.* 45, 1198 (1972).
36. Sawada M., Tsuno Y., Yukawa Y.: *Bull. Chem. Soc. Jap.* 45, 1207 (1972).
37. Taft R. W.: *J. Amer. Chem. Soc.* 74, 3120 (1952).
38. Taft R. W.: *J. Amer. Chem. Soc.* 75, 4231 (1953).
39. Taft R. W.: *J. Amer. Chem. Soc.* 75, 4538 (1953).
40. Pavelich W. H., Taft R. W.: *J. Amer. Chem. Soc.* 79, 4935 (1957).

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