Tetrahedron. Vol. 28, pp. 1325 to 1329. Pergamon Press 1972. Printed in Great Britain

A NOTE ON THE EXTENDED HAMMETT EQUATION FOR RADICAL REACTIONS

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(*Received in the UK* 11 *November* 1971; *Accepted for publication* 19 *November* 1971)

Abstract—A critical examination of the extended Hammett equations proposed for radical reactions is presented. It is shown that the resonance parameters are in error and that the use of these relations may bring about false conclusions concerning the mechanism of the reaction studied. It is concluded that no justification exists for the use of a special linear free energy relation in the case of radical reactions.

INTRODUCTION

IN RECENT YEARS several investigators[1–3] have proposed an extended Hammett equation of the general form

$$\log(k/k^0) = \rho\sigma + \beta \tag{1}$$

in order to correlate substituent effects in radical reactions. Here, ρ and σ are the reaction and substituent constants, respectively, whereas β accounts for the extra stabilization due to resonance interactions of *para* substituents with the reaction center. If these relations have to be considered as a useful tool to elucidate whether or not a radical mechanism is operative, they must be distinguishable from linear free energy relations used for heterolytic reactions.[4] Both this aspect and the way of defining the parameters used give rise to serious objections to these relations, which will be outlined in this paper on the basis of the equation proposed by Yamamoto and Otsu.[2]

RESULTS AND DISCUSSION

Yamamoto and Otsu proposed for radical reactions the relation[2]

$$\log(k/k^0) = \rho\sigma + \gamma E_R \tag{2}$$

in which E_R is the resonance parameter for *para* substituents and γ denotes the susceptibility of the resonance effects. The authors do not define which σ constants have been used in this relation, despite the fact that E_R will clearly be dependent on the choice of σ. From Fig 1 in their article, it can be seen that the σ values of McDaniel and Brown[5] and/or those of Jaffé[6] have been applied. Since these σ values are based on (or correspond closely with) dissociation data of benzoic acids in water, they include the exaltation arising from the difference in mesomeric *para* interaction of the carboxyl group and the carboxylate anion with +M substituents.[7] Therefore, the E_R values are surely affected by this heterolytic resonance interaction.

Assuming the use of primary σ_m values[7] by Yamamoto and Otsu for the determination of $\rho = +0{\cdot}7$ for their standard reaction (H· abstraction from substituted cumenes with $\gamma = 1$), we have calculated E_R values which are free from this heterolytic resonance interaction. These new E_R values, denoted as E_R^n for convenience, are then defined by

$$E_R^n = \log(k/k^0) - \rho\sigma^n \text{ with } \rho = +0{\cdot}7 \tag{3}$$

so that

$$E_R^n = E_R + 0{\cdot}7\,(\sigma - \sigma^n) \tag{4}$$

Table 1 shows the results of these E_R^n values. In the case of discrepancy between σ (McDaniel and Brown) and σ (Jaffé), the latter and the corresponding E_R^n values are put in parentheses

TABLE 1. COMPARISON OF E_R AND CALCULATED E_R^n VALUES

Substituent	σ[a]	σ^n[b]	E_R[c]	E_R^n
4-$N(CH_3)_2$	−0·83 (−0·600)[d]	−0·33[e]	0·24	−0·11 (0·05)[f]
4-OH	−0·370 (−0·357)[d]	−0·17[e]	0·17	0·030 (0·039)[f]
4-OCH_3	−0·268	−0·100	0·11	−0·008
4-OC_6H_5	−0·320 (−0·028)[d]	0·076	0·13	−0·147 (0·057)[f]
4-CH_3	−0·170	−0·124	0·03	−0·002
4-isoC_3H_7	−0·151	−0·156	0·03	0·034
4-*tert*-C_4H_9	−0·197	−0·174	0·03	0·014
H	0	0	0	0
4-Cl	0·227	0·281	0·10	0·062
4-Br	0·232	0·30	0·12	0·072
4-I	0·180 (0·276)[d]	0·299	0·12	0·037 (0·104)[f]
4-$COCH_3$	0·502 (0·516)[d]	0·502	0·24	0·24 (0·25)[f]
4-CN	0·660 (0·628)[d]	0·674	0·24	0·23 (0·21)[f]
4-NO_2	0·778	0·778	0·41	0·41

[a] Ref[5] [b] Ref[4, 7] [c] Ref[2] [d] Different values of Jaffé[6]
[e] Mean values from ref[4, 7] [f] Calculated using σ (Jaffé)

The data show that the E_R^n values of the +M substituents are rather small and indefinite of sign. In particular, the picture for the strong electron-donating substituents like $N(CH_3)_2$, OH, OCH_3, and OC_6H_5 indicates that the origin of E_R is solely the "normal" $\sigma - \sigma^n$ exaltation. This suspicion against the E_R parameter may further be demonstrated using the Yukawa approach of the Hammett equation[4]

$$\log(k/k^0) = \rho(\sigma^n + r^+\,\Delta\bar{\sigma}_R^+) \tag{5}$$

in which r^+ and $\Delta\bar{\sigma}_R^+$ are the reaction and substituent resonance parameters, respectively. For +M substituents in the benzoic acid dissociation in water this relation yields[4]

$$\sigma = \sigma^n + 0{\cdot}272\,\Delta\bar{\sigma}_R^+ \quad (r = 1{\cdot}000) \tag{6}$$

in which r denotes the correlation coefficient.

Combining equations (4) and (6) in addition to $E^n_R \approx 0$ gives

$$E_R \approx -0{\cdot}19\,\Delta\bar{\sigma}^+_R \qquad (7)$$

while correlation of E_R with $\Delta\bar{\sigma}^+_R$ for OH, OCH_3, OC_6H_5,* $N(CH_3)_2$, t-C_4H_9, isoC_3H_7, CH_3, and H yields

$$E_R = -0{\cdot}184\,\Delta\bar{\sigma}^+_R + 0{\cdot}006 \quad (r = 0{\cdot}988) \qquad (8)$$

So the physical meaning of E_R is identical with that of $\Delta\bar{\sigma}^+_R$ for these +M substituents. The correlation of (8) is poor ($r = 0{\cdot}859$) when the halogens are included. In accordance with the results of Walter,[9] the halogens show a much greater resonance interaction than might be expected as follows from†

$$E_R = -0{\cdot}694\,\Delta\bar{\sigma}^+_R + 0{\cdot}002 \quad (r = 0{\cdot}973) \qquad (9)$$

for these substituents. This phenomenon, however, has to be studied throughout before one may accept this as a general feature of radical reactions. It may be noted, that the σ^+_{IP} values, proposed recently for ionisation potential measurements in mass spectrometry,[10] also point to a much greater resonance interaction in the case of the halogens as substituents.

In contrast to the +M substituents, the E^n_R values for −M substituents differ just slightly from E_R. The E_R values of the −M substituents, however, may be well correlated with their respective heterolytic exaltations, i.e. $\Delta\bar{\sigma}^-_R = \sigma^- - \sigma^n$,‡ as can be seen from

$$E_R = 0{\cdot}787\,\Delta\bar{\sigma}^-_R - 0{\cdot}012 \quad (r = 0{\cdot}982) \qquad (10)$$

Hansch and Kerley[11] found that E_R could not be correlated by the Swain and Lupton equation[12]

$$E_R = fF + rR \qquad (11)$$

in which the parameters F and R denote the inductive-field and resonance effects of the substituents and f and r are the weighting factors for these effects, respectively. However, the demonstrated complex nature of E_R prevents *a priori* a relationship of this type. Consequently, one has to consider the +M and −M substituents separately for such a correlation. For +M substituents we obtain

$$E_R = 0{\cdot}074\,F - 0{\cdot}168\,R + 0{\cdot}016 \quad (r = 0{\cdot}908) \qquad (12)$$

or, leaving out the halogens,

$$E_R = -0{\cdot}126\,F - 0{\cdot}354\,R - 0{\cdot}017 \quad (r = 0{\cdot}985) \qquad (13)$$

whereas the −M substituents are correlated by

$$E_R = 0{\cdot}312\,F + 0{\cdot}197\,R + 0{\cdot}002 \quad (r = 0{\cdot}965) \qquad (14)$$

These relations demonstrate further both the different behavior of the halogens and the quite divergent nature of E_R for +M and −M substituents.

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* For 4-OC_6H_5 was used $\Delta\bar{\sigma}^+_R = -0{\cdot}576$, calculated from σ^+ and σ^n from ref[8,4]

† For 4-I was used $\Delta\bar{\sigma}^+_R = -0{\cdot}164$, calculated from σ^+ and σ^n from ref[8,7]

‡ $\Delta\bar{\sigma}^-_R$ calculated from σ^- and σ^n from ref[6,7]

In contrast to the Swain and Lupton parameters, σ and σ^+ are able to correlate E_R for all the substituents as shown by Hansch and Kerley*[11]

$$\sigma^+ = -1{\cdot}323\,E_R + 1{\cdot}601\,\sigma - 0{\cdot}016 \quad (r = 0{\cdot}989) \tag{15}$$

At first sight, this type of relation should exist just in the case of +M substituents because of the identical character of the Yamamoto and Otsu relation (2) and the Hammett–Yukawa treatment (5) for these substituents. In this way, combination of Eqns (2), (5) and (6) yields

$$\sigma^+ = \left[\frac{\gamma}{1{\cdot}37\,\rho\sigma^+ - 0{\cdot}37\,\rho}\right]E_R + \sigma \tag{16}$$

which is of the same nature as that of Eqn (15).

The fact that −M substituents also obey relation (15) has to be ascribed to empiric coincidence, because σ and σ^- for the −M substituents are well correlated by

$$\sigma^- = 1{\cdot}582\,\sigma + 0{\cdot}013 \quad (r = 0{\cdot}994) \tag{17}$$

whereas for −M substituents

$$\sigma \approx \sigma^+ \approx \sigma^n \tag{18}$$

Combining Eqns (15), (17) and (18) gives

$$E_R \approx 0{\cdot}75\,\Delta\bar{\sigma}_R^- \tag{19}$$

which is in excellent agreement with the correlation found by Eqn (10).

CONCLUSIONS

In conclusion, we may state that the proposal of Yamamoto and Otsu to use special E_R values in the case of radical reactions is not justified. Moreover, the γ and E_R parameters are in error, so that the use of their relation may bring about false conclusions concerning the mechanism and the transition state of the reaction studied. For instance, $\gamma = 1$ would imply a significant resonance interaction between all the *para* substituents and the reaction center. In fact, this is just true in the case of −M substituents. The success of Yamamoto and Otsu in correlating numerous of data is well understood, because virtually the following Hammett–Yukawa treatment has been applied[12]

$$\log(k/k^0) = \rho(\sigma^n + r^+\Delta\bar{\sigma}_R^+ + r^-\Delta\bar{\sigma}_R^-) \tag{20}$$

which appears from combination of Eqns (2), (8) and (10). The standard reaction chosen by Yamamoto and Otsu will obey this relation with $\rho = +0{\cdot}7$, $r^+ = 0$, and $r^- = +1{\cdot}1$.

All these objections are equally applicable to the relations for radical reactions of Simamura *et al.*[1] and of Sakurai *et al.*[3], because of the mutually identical nature of all these relations.

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* These authors have also included E_R values of obscure origin for 3-Cl, 3-CH_3, and 3-NO_2 in this relation, despite the fact that the Yamamoto and Otsu treatment assumes $E_R = 0$ for all *meta* substituents. Leaving out these substituents, however, has hardly any influence on the relation given.

Acknowledgement—I thank Professor H. van Bekkum for his interest and encouragement.

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