

Resonance Effect in Hammett Relationship. I. The Substituent Effect in the Acid Catalyzed Decompositions of ω -Diazoacetophenones in Acetic Acid

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As reported in a previous paper, the Curtius rearrangement of substituted benzazides in toluene did not give a linear Hammett relationship¹⁾, whereas, the decomposition catalyzed by sulfuric acid²⁾ showed an approximately linear one, which had the negative ρ value. In such an electrophilic reaction, as has been pointed out frequently³⁻⁷⁾, electron releasing para substituents would favor the rate to a greater extent than would be expected from the normal Hammett constants. The same may be anticipated in this reaction. *p*-Hydroxyl and *p*-methoxyl groups indicated the tendency of some higher acceleration, but the scatters of the other groups, especially *p*-nitro group, made it impossible to ascertain this trend. The detailed re-examination as never improved the result. The acid catalyzed solvolytic decomposition of ω -diazoacetophenones is an electrophilic reaction of similar type. Hence, one might anticipate that para substituted derivatives probably show a similar behavior to what is seen in other electrophilic reactions. Furthermore, the rate changes of this reaction might suggest the contribution of substituents at least in such a reaction of which the substituent effects are transmitted through a carbonyl group to an electron deficient reaction center. Lane and coworkers⁸⁾, in their study of the substituent effect of this reaction, reported that the rate fitted the Hammett equation, whereas the effect of strongly electron releasing groups has not

been reported. Therefore, kinetic study of decomposition of various substituted ω -diazoacetophenones was carried out in acetic acid, and the results are discussed on the basis of the Hammett relationship.

Experimental

Materials.—Substituted and unsubstituted diazoacetophenones used in this investigation were prepared by the usual procedure^{8,9)}; all benzoyl chlorides reacted satisfactorily with an excess of diazomethane in ethereal solution with cooling. After this solution was allowed to stand overnight at room temperature, the solvent was removed in vacuo and the residue was collected. Several recrystallizations from ligroin or benzene solution gave pale yellow crystals. The melting points of the diazoketones thus obtained are listed in Table I, together with the boiling points of the starting benzoyl chlorides.

Solvent.—Acetic acid was purified by the same method as that described in a previous paper²⁾; b. p. 117.5–118.0°C.

Kinetic Experiments.—The rates of decompositions were determined in 75 ml. of anhydrous acetic acid at 40.00 \pm 0.01°C, by collecting the evolved nitrogen by an azotometer. The procedure and the apparatus were the same as those described in several recent papers^{1,2,8)}. The solution was not stirred but powdered glass was added to the solution in order to prevent the supersaturation of nitrogen gas evolved. In each run, the initial concentration of diazoketone was about 1/200 mol. Volume readings were taken covering the extent of 75% completion of reaction. The infinity reading was determined at the time after a period of 9–10 times as much as the half life of the reaction. The measurements were repeated at least three times for respective diazoketones in order to minimize the experimental error. The total volume of nitrogen collected was close to the theoretical amount. The change in the initial concentration did not show any effect on the rate.

Reaction Product.—The reaction solution was allowed to remain at 40.00°C in a bath until no further evolution of nitrogen occurred, and then the solvent was removed in vacuo. The

1) Y. Yukawa and Y. Tsuno, *J. Am. Chem. Soc.*, **79**, 5530 (1957).

2) Y. Yukawa and Y. Tsuno, *ibid.*, **81**, 2007 (1959).

3) C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951).

4) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

5) (a) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955); (b) N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957).

6) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

7) J. Miller, *Australian J. Chem.*, **9**, 61 (1956).

8) J. F. Lane and R. L. Feller, *J. Am. Chem. Soc.*, **73**, 4230 (1951).

9) W. E. Bachmann and W. S. Struve, "Organic Reactions", Vol. 1, John Wiley & Sons, Inc., New York (1942), p. 38.

TABLE I. ω -DIAZOACETOPHENONES, BENZOYL CHLORIDES AND THE DECOMPOSITION PRODUCTS

Subst.	Melting point and boiling point ^{a)} (°C)		
	$\text{XC}_6\text{H}_4\text{COCl}$	$\text{XC}_6\text{H}_4\text{COCHN}_2$	$\text{XC}_6\text{H}_4\text{COCH}_2\text{Ac}$
H	(192~192.7)	47.2~48.0 ^{b)}	48
<i>p</i> -CH ₃ O	(152~155/20 mm.)	87.5~88.5 ^{c)}	57.5~58.5
<i>p</i> -C ₂ H ₅ O	(161/27 mm.)	80.0~80.5 ^{d)}	86.0~86.8
<i>p</i> - <i>t</i> -C ₄ H ₉	(149.9~150.5/14 mm.)	83.5~84.0 ^{e)}	60.5~61.3
<i>p</i> -CH ₃	(122/33 mm.)	52.0~52.8 ^{b)}	84.0~85.0
<i>p</i> -C ₆ H ₅	112.5~113.0	119.0~119.5 ^{f)}	112.0~112.8
<i>p</i> -Cl	(120~121/28 mm.)	114.0~115.0 ^{b)}	68.5~69.0
<i>p</i> -Br	(139.0~139.5/33 mm.)	126.0~126.5 ^{b)}	85.8~86.5
<i>p</i> -NO ₂	72.7~73.3	118.0~119.0 ^{b)}	122~123.5
<i>m</i> -CH ₃	(116~117/30 mm.)	64.2~64.8 ^{g)}	liquid
<i>m</i> -Br	(138.5~139.5/38 mm.)	73.5~75.0 ^{h)}	liquid
<i>m</i> -NO ₂	(169.0/20 mm.)	139.5~140.0 ⁱ⁾ (decomp.)	48.5~49.0

a) All melting points are corrected. Boiling points which are given in brackets are uncorrected.

b) J. F. Lane et al., Ref. 8.

c) M. S. Newman and P. Beal, III, *J. Am. Chem. Soc.*, **71**, 1506 (1949).

d) *Anal.* Found: C, 63.56; H, 5.35; N, 14.84%.

Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2$: C, 63.16; H, 5.31; N, 14.74%.

e) *Anal.* Found: C, 71.33; H, 6.53; N, 14.17%.

Calcd. for $\text{C}_{12}\text{H}_{14}\text{ON}_2$: C, 71.26; H, 6.98; N, 13.85%.

f) C. E. Blades and A. L. Wilds, *J. Org. Chem.*, **21**, 1013 (1956).

g) *Anal.* Found: C, 67.11; H, 5.21; N, 16.21%.

Calcd. for $\text{C}_9\text{H}_9\text{ON}_2$: C, 67.48; H, 5.03; N, 17.49%.

h) *Anal.* Found: C, 43.01; H, 2.34; N, 12.32%.

Calcd. for $\text{C}_8\text{H}_5\text{ON}_2\text{Br}$: C, 42.66; H, 2.22; N, 12.44%.

i) *Anal.* Found: C, 51.02; H, 2.84; N, 20.60%.

Calcd. for $\text{C}_8\text{H}_5\text{O}_3\text{N}_3$: C, 50.26; H, 2.62; N, 21.99%.

residues were recrystallized several times from ligroin or ethanol solutions. The corresponding phenacyl acetates having sharp melting points were obtained in quantitative yield (Table I). In the case of *m*-CH₃ and *m*-Br derivatives, the residues were not solidified.

Results and Discussion

The evolution of nitrogen followed strictly the first order equation

$$0.4343 \times kt = \log V_{\infty} - \log (V_{\infty} - V)$$

where V_{∞} is the volume reading at the infinite time and V the readings at time t . Typical runs of the evolution of nitrogen are given graphically in Fig. 1. The rate constants obtained at 40.00°C are listed in Table II. The average deviations less than 0.7% are obtained in respective runs and the reproducibility of the results is estimated to be about 1%. Some of the rate constants obtained in the present study are slightly lower than those obtained by Lane et al.⁸⁾ This appears to be attributable to the difference of acetic

acid used as solvent or that of the methods evaluating rate constants.

The mechanism of this reaction proposed is possibly represented as follows:

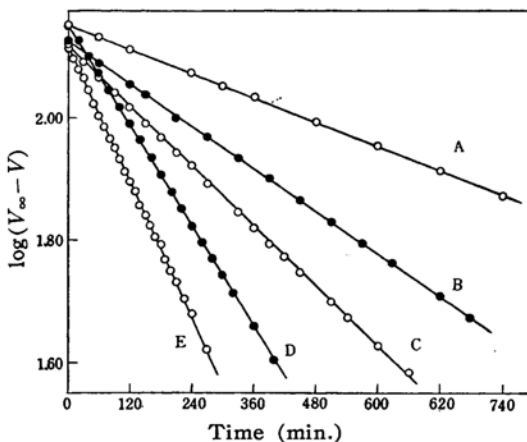


Fig. 1. Typical first order plots for the decomposition of substituted ω -diazoacetophenones in acetic acid at 40.00°C. A, *m*-NO₂; B, *m*-Br; C, *p*-Cl; D, *m*-CH₃; E, *p*-CH₃.

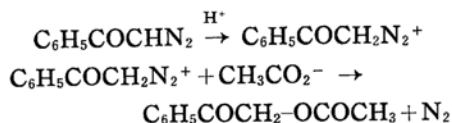
TABLE II. THE RATE CONSTANTS OF THE DECOMPOSITION OF SUBSTITUTED ω -DIAZOACETOPHENONES IN ACETIC ACID AT 40.00°C

Subst.	$10^3 \times k_1^a$	Subst.	$10^3 \times k_1^a$
<i>p</i> -CH ₃ O	7.76 ± 0.06	<i>p</i> -Br	1.91 ± 0.02
<i>p</i> -C ₂ H ₅ O	7.37 ± 0.07	None	2.74 ± 0.02^c
<i>p</i> -CH ₃	4.33 ± 0.04^b	<i>m</i> -CH ₃	3.14 ± 0.04
<i>p</i> - <i>t</i> -C ₄ H ₉	4.12 ± 0.04	<i>m</i> -Br	1.32 ± 0.02
<i>p</i> -C ₆ H ₅	3.37 ± 0.02	<i>m</i> -NO ₂	0.744 ± 0.007
<i>p</i> -Cl	1.98 ± 0.01	<i>p</i> -NO ₂	0.600 ± 0.006

a) Rate in reciprocal minute.

b) Reported 4.88×10^{-3} at 40.05°C by Lane et al., Ref. 8.

c) Reported 2.94×10^{-3} , Ref. 8.



the first step is the protonation (presumably reversible process) of diazoketone and the second is the rate determining decomposition of the protonated ketodiazonium ion to the acetate. With regard to the second step, two types of mechanism are possible; one is the unimolecular loss of nitrogen followed by the reaction with solvent of the carbonium ion so produced, another is the bimolecular reaction with solvent or acetate ion. Lane et al. suggested the latter one⁸).

It will be of interest to discuss the substituent effects on the basis of the Hammett equation¹⁰). As is shown clearly

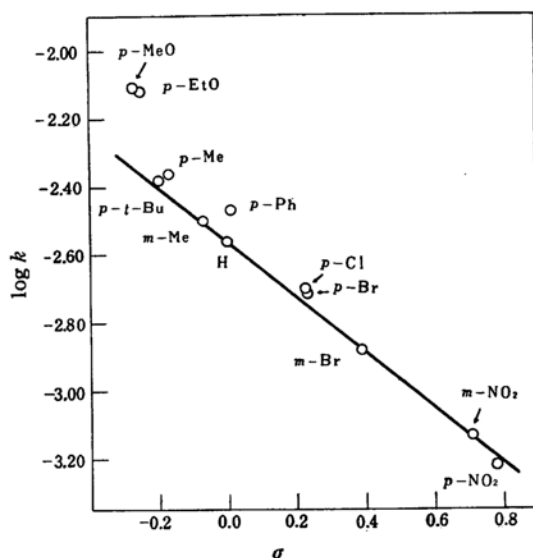
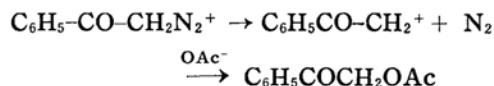


Fig. 2. The Hammett equation applied to the decomposition of ω -diazacetophenones in acetic acid at 40.00°C.

in Fig. 2, the plot of $\log k$ against the corresponding Hammett σ -constants fails to give a linear relationship but concaves upward, in contrast to the result by Lane et al.⁸) Only with respect to meta substituents and the *p*-nitro group, the linear correlation is obtained. The slope of this correlation line, the ρ_m value, is evaluated using the method of least squares¹¹) to be -0.830 , the probable error of the fit 0.010 in $\log k$ and the correlation coefficient 0.999 . On the other hand, the plots of $\log k$ vs. σ for para groups lie substantially above the meta line. The deviations appear to be entirely significant in view of the experimental uncertainty.

The above results are not unusual but may be reasonable at least in qualitative consideration. Although the Hammett equation correlates the rates or equilibria of an enormous number of reactions^{10,11}), some limitations have been noted. One of the limitations is the electrophilic reactions providing the deviations of the plots for electron releasing para substituents such as methoxy, methyl, phenyl and halo groups. In general, these groups show greater electron-release than described by the normal σ -constants in an electrophilic reaction³⁻⁷). The upward curvature of the plots for these groups is reasonably attributed to differing capacities of the substituents for resonance stabilization of a positively charged transition state. The same considerations as noted above might be employed in the case of the present reaction. If the upward deviations are referred to the resonance capacities, the transition state of this reaction must have a positively charged reaction center, and the charge must be, if possible, delocalized through resonance interaction. This appears to suggest that the driving force of the present reaction may be the elimination of the nitrogen molecule, followed by the attack of acetate ion upon the carbonium ion so produced.

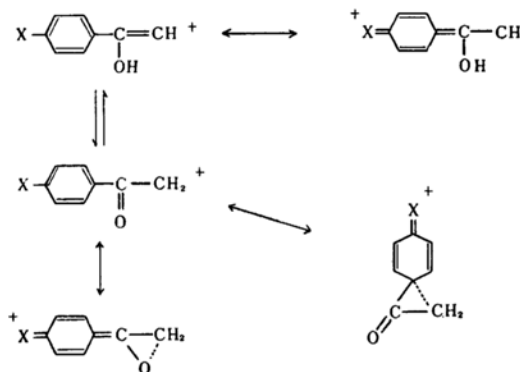


Although this is somewhat inconsistent with Lane's conclusion, this consideration might be reasonable because the decomposition of the diazonium ion into nitrogen and carbonium ion undoubtedly does not

10) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937); "Physical Organic Chemistry", McGraw-Hill Book Co., Inc., New York (1940), p. 194.

11) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

have high energy requirements¹²). At least the pull factor of the leaving nitrogen may predominate over the push of the attacking species, because of the high stability of the nitrogen molecule. The positive charge so produced at the reaction center would be delocalized through the resonance with powerfully electron releasing aryl groups;



These are consistent with the present data qualitatively. Then, it will be of further interest to treat the deviations in quantitative manner.

The Quantitative Treatment.—The recent advance in this field has prompted us to some attempts to correlate electrophilic reactions with an alternative set of substituent constants. These new substituent constants are denoted by σ^+ ¹³. Although a number of tentative sets of σ^+

have been proposed by various authors, it is Brown and Okamoto's set⁵) that is apparently the most decisive one of general applicability. In Fig. 3 is demonstrated the correlation of present data with Brown and Okamoto's set of σ^+ . Least squares treatment¹¹) indicates that the ρ^+ value, the slope of the regression line, is equal to -0.736 ± 0.0246 , the correlation coefficient being 0.994. Brown and Okamoto's set of σ^+ correlates the present data more appropriately than does the normal Hammett constant, whereas it is worthy of remark that all the points for para substituents fall below the ρ_m line to a considerable extent. The ρ^+ value is clearly lower than ρ_m value. This would indicate that the σ^+ values employed for para substituents somewhat overcorrect the present situation. Furthermore, it might possibly be attributed to less availability of the transition state resonance of the present reaction than that described on the basis of σ^+ . However, this is not surprising, because the contribution of resonance would not always be constant but would vary from reaction to reaction. Such failure of the linear relationship using the set of σ^+ is frequently observed. Some of the examples are provided by the solvolysis of neophyl brosylates¹⁴) in which the resonance effect is less effective than described by Brown and Okamoto's σ^+ values, and the brominolysis of benzeneboronic acids¹⁵) in which the contribution of transition state resonance appears greater

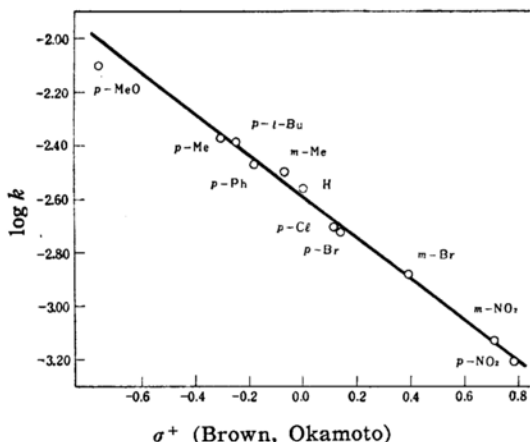


Fig. 3. Plot of decomposition rates of ω -diazacetophenones against Brown and Okamoto's σ^+ .

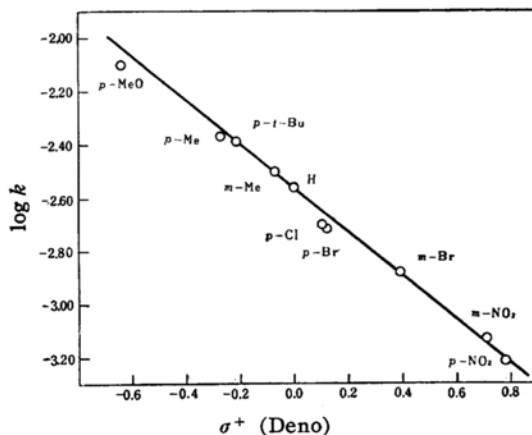


Fig. 4. Correlation of rates of the decomposition of ω -diazacetophenones with Deno's σ^+ .

12) A. Streitwieser, Jr. and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957); A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

13) See reference (22) in Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

14) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3432 (1957).

15) H. G. Kuivila and A. R. Hendrickson, *ibid.*, **74**, 5069 (1952); H. G. Kuivila and L. E. Benjamin, *ibid.*, **77**, 4834 (1955).

than the estimated. Hence, it is the existence of a unique set of σ^+ that would be rather surprising in itself.

On the other hand, through Deno's set of σ^+ ⁵⁾ the present data can be correlated more successfully than through Brown

and Okamoto's, as shown in Fig. 4. The ρ^+ value of this correlation is equal to -0.789 ± 0.024 , the correlation coefficient being 0.996. It is evident that the points for para substituents come closer to fitting on the ρ_m line, while the ρ^+ value is not strictly equal to the ρ_m value. The set defined by Pearson from the Beckmann rearrangement¹⁶⁾ also gives a rather more satisfactory result for the present reaction than does Brown and Okamoto's set, although this has not been reported to show any applicability. These facts appear to indicate that the respective sets of σ^+ may be applicable only to respective limited regions of electrophilic reaction series. Then, it would be by no means meaningless to set up tentative σ^+ values from the present reaction. This is encouraged by the success of linear free energy relationship between present data

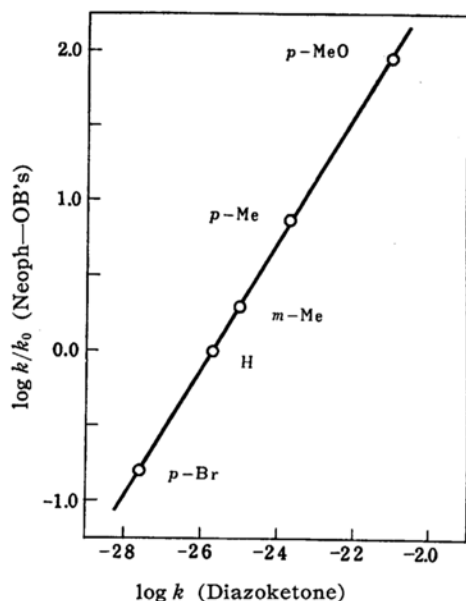


Fig. 5. Correlation of rates of acetolysis of neophyl brosylates and decomposition of ω -diazoacetophenones.

TABLE III. SUBSTITUENT CONSTANTS USED FOR CORRELATING RATES OF DECOMPOSITION OF THE ω -DIAZOACETOPHENONES

Substituent	Hammett ^{a)}	Brown ^{b)}	Deno ^{c)}	σ^+ ^{d)}
<i>p</i> -CH ₃ O	-0.268	-0.764	-0.64	-0.537
<i>p</i> -C ₂ H ₅ O	-0.250			-0.512
<i>p</i> - <i>t</i> -C ₄ H ₉	-0.197	-0.250	-0.21 ^{f)}	-0.209
<i>p</i> -CH ₃	-0.170	-0.306	-0.27	-0.234
<i>p</i> -C ₆ H ₅	+0.009	-0.179		-0.103
None	0.000	0.000	0.00	0.000
<i>p</i> -Cl	+0.227	+0.112	+0.11 ^{g)}	+0.175
<i>p</i> -Br	+0.232	+0.148		+0.202

- a) Taken from the compilation by Jaffé (Ref. 11).
 b) Brown and Okamoto's set of σ^+ (Ref. 6).
 c) Deno's set of σ^+ (Ref. 5a).
 d) The σ^+ values obtained from the present data. These were calculated from the Hammett equation using $\rho = \rho_m = -0.830$ and $\log k_0 = -2.558$.
 e) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
 f) The value derived from the dissociation of benzhydrols (Ref. 5b).
 g) The value taken from Ref. 5b. In the original paper (Ref. 5a) +0.08 was given, while the quoted value, +0.11, appears to be more suitable.

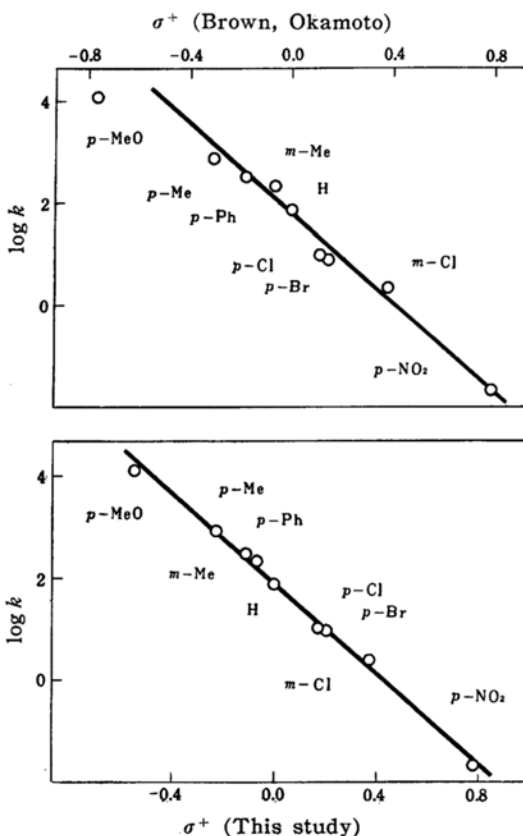


Fig. 6. Correlations of the Beckmann rearrangement of acetophenonoximepicrylethers with Brown and Okamoto's and our σ^+ values.

16) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952); D. E. Pearson and J. D. Burton, *ibid.*, **19**, 957 (1954).

and the solvolysis rates of neophyl brosylates¹⁴⁾, as shown in Fig. 5. The new set of σ^+ is given in Table III, along with the values of other sets of substituent constants. The present set does not appear to be applicable to a great many reactions. In some cases, however, it does describe a better correlation than does Brown and Okamoto's. Fig. 6 exhibits the correlations of the Beckmann rearrangement of acetophenone oxime picryl ethers¹⁷⁾ with the present set and with Brown and Okamoto's σ^+ . Some other reactions which are satisfactorily correlated by the present set are as follows: the acetolysis of neophyl brosylates¹⁴⁾, the Beckmann rearrangement of acetophenonoximes¹⁶⁾, Diels-Alder reaction of 1-phenyl-1,3-butadienes with maleic anhydride¹⁸⁾ and acid catalyzed rearrangement of phenylpropenylcarbinols¹⁹⁾.

A particular interest is seen in Table III. For each substituent, σ^+ values become more negative in the following order; the present set < Deno's < Brown and Okamoto's. The correction relative to the normal substituent constant is great in magnitude in Brown and Okamoto's, small in Deno's and smaller in the present set of σ^+ . This parallels presumably the degree of resonance stabilization of elec-

tron deficient transition states in respective reference reactions, if the other factors remain constant throughout respective substituted derivatives. Thus, the resonance contribution of substituents would be more important in Brown and Okamoto's reference reaction than in Deno's and of even greater importance than in the present reaction. This is consistent with the facts that in Deno's reference reaction, the dissociation of triphenylcarbinols, the charge delocalization is shared separately by three aryl groups and in the present reaction the resonance contribution of a substituent group is reduced through the carbonyl group.

All one can say is that the σ^+ is not essentially constant but variable with respect to the change in reaction. ρ — σ^+ equation should be applied to the limited reaction series in which the availability of *transition state resonance* is equivalent to that in respective reference reactions. Now, it is highly desirable to correlate these sets of σ^+ with a simple relationship, which will be described in Part II.

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17) R. Huisgen, J. Witte, H. Walz and W. Jira, *Ann.*, **604**, 191 (1957).

18) E. J. Dewitt, C. T. Lester and G. A. Ropp, *J. Am. Chem. Soc.*, **78**, 2101 (1956).

19) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, **1947**, 1096.