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The Wolff Rearrangement. II. The Substituent Effects on the Rate of the Catalytic Decomposition of Substituted α-Diazoacetophenones

Yasuhide YUKAWA, Yuho TSUNO and Toshikazu IBATA[*1]

The Institute of Scientific and Industrial Research, Osaka University, Higashiasakayama, Sakai, Osaka

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The substituent effect on the reaction rates of the Wolff rearrangement of meta- and para-substituted α-diazoacetophenones was studied in *t*-butyl alcohol, isopropyl alcohol, and *t*-butyl alcohol - toluene mixed solvents, and also on the decomposition rates in toluene, using a solution of silver benzoate in triethylamine as a catalyst. Similar substituent effects were observed regardless of the solvents used. Strong electron-releasing conjugative substituents at the para position, such as methoxy and ethoxy groups, retard the reaction rate greatly. The other substituents accord roughly with the Hammett relationship, having small negative ρ-values. The decomposition rate constants in toluene were apllicable to the Yukawa-Tsuno equation, which has a negative r-value:

$$\log k/k_0 = -0.45(\sigma - 2.7\Delta\sigma_R{}^+) - 0.05$$

proving that the resonance stabilization on the reaction origin are caused by the electron-releasing substituent at the para position. The results of the kinetic isotope effects (no apparent kinetic isotope effect was observed within the range of experimental error) of the Wolff rearrangement of carbonyl-^{14}C, and phenyl-1-^{14}C labeled α-diazoacetophenone under the same reaction conditions favor the two-step mechanism to the concerted one for the elimination of nitrogen and the migration of the alkyl group.

Many papers published hitherto on the Wolff rearrangement[1)] have concentrated on the region of the synthetic method of carboxylic acid derivatives. A ketocarbene-ketene mechanism[2-4)] has long been applied to the catalytic, photochemical, and thermal Wolff rearrangements by analogy to the Curtius rearrangement.

However, no kinetic study of the Wolff rearrangement has been published because of the heterogeneity of the ordinarily-used catalysts, such as silver oxide. On finding a homogeneous catalyst, silver benzoate in triethylamine, a free-radical-chain mechanism was proposed by Newman and Beal[5)] for the rearrangement. In a previous paper[6)] we have reported on a kinetic study of the Wolff rearrangement, catalyzed by Newman's catalyst, and proposed a mechanism containing the silver ion-complex as the real entity of the catalyst.

In order to ascertain this mechanism, the substituent effect on the Wolff rearrangement of meta- and para-substituted α-diazoacetophenones was studied using the same catalyst in isopropyl alcohol, *t*-butyl alcohol, and a mixed *t*-butyl alcohol and toluene solvent; in addition, we studied the substituent effect on the decomposition of diazoketones in toluene. The reaction mechanism will be discussed in view of the similarity of the substituent effect of the Wolff rearrangement to that of the Curtius rearrangement[7)] of the isoelectronic benzazides.

Experimental

Materials. *The Substituted and Unsubstituted α-Diazoacetophenones* used in this investigation were prepared in the usual method.[8)] Benzoyl chlorides were stirred, drop by drop, into an ethereal solution of three molar amounts of diazomethane, prepared by the alkaline decomposition of *N*-nitroso-*N*-methylurea below 0°C. After leaving the reaction mixture stand overnight at room temperature, the solvent was removed *in vacuo* and the residue was recrystallized several times from a ligroin or benzene solution. The melting points of diazoketones are listed in Table 1.

The Silver Benzoate was prepared by a method previously described.[6)]

[*1] Present address: Department of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka

1) W. E. Bachmann and W. S. Struve. "Organic Reactions," Vol I, John Wily & Sons, Inc., New York (1942), p. 39.

2) L. Wolff, *Ann.*, **394**, 23 (1912).

3) W. Kirmse, "Carbene Chemistry," Academic Press, New York (1964).

4) J. Hine, "Divalent Carbon," Ronald Press, New York (1964), p. 140.

5) M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

6) Y. Yukawa, Y. Tsuno and T. Ibata, This Bulletin, **40**, 2613 (1967).

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

8) Y. Tsuno, T. Ibata and Y. Yukawa, This Bulletin, **32**, 960 (1959).

Table 1. α-Diazoacetophenones and phenylacetic acids

Substituent	Diazoketone mp, °C	Acid mp, °C
p-CH_3O	87.5— 88.5	86.8— 87.8
p-C_2H_5O	80.0— 80.5	88.6— 89.0
p-t-C_4H_9	83.5— 84.0	
p-CH_3	52.0— 52.8	92.0— 93.0
m-CH_3	64.2— 64.8	60.5— 61.5
H	47.2— 48.0	77.0— 78.0
p-C_6H_5	119.0—119.5	162.0—163.0
p-Cl	114.0—115.0	102.0—103.0
p-Br	126.0—126.5	114.0—115.0
m-Br	73.5— 75.0	
m-NO_2	139.5—140.0	119.0—120.0
p-NO_2	118.0—119.0	151.5—152.0

Isopropyl Alcohol, t-Butyl Alcohol, and Triethylamine. These solvents were purified by method described before.6)

isopropyl alcohol	bp 82.3—82.5°C
t-butyl alcohol	bp 82.5—82.7°C
triethylamine	bp 87.9—88.0°C

Toluene. Commercial toluene was purified by the usual method; it was distilled after having been refluxed several tens of hours over metallic sodium in order to remove a trace of water dissolved.7) bp 110.0—111.0°C.

Kinetic Measurements. The reaction was carried out using 5.0 mmol of diazoketones, 0.100 g (0.44 mmol) of silver benzoate, 2.0 m*l* (*ca.* 15 mmol) of triethylamine, and 100 m*l* of the solvent. The reaction rates were determined according to a procedure described previously6) by collecting the evolved nitrogen gas in an azotometer.

Reaction Products in an Alcoholic Solution. When a reaction was over, an almost quantitative volume of nitrogen was collected. The reaction products were identified as the corresponding substituted phenylacetic acids by the alkaline hydrolysis of the residue, as has been described in a previous paper.6) The melting points of the acids are shown in Table 1.

Reaction Products in Toluene Solution. As Table 3 shows, the volume of nitrogen evolved was not quantitative with respect to some diazoketones, namely, *p*-phenyl-, *p*-chloro-, *p*-bromo-, *p*-nitro-, *m*-bromo-, and *m*-nitro-α-diazoacetophenones. In these cases, toluene was removed *in vacuo* after the evolution of nitrogen had ceased, and the residue was cooled in a refrigerator. A small amount of crystals was separated from oily substance by filtration after recrystallization from ligroin or benzene; the crystalline substance was identified as recovered diazoketones by a comparison of the IR spectra and melting points with those of authentic samples. From the oily layer no pure substance was obtained by vacuum distillation. Similarily, only a tarry substance was obtained from the reaction mixture of other diazoketones. When a large-scale reaction was carried out, benzoic acid was obtained from silver benzoate, while 3-benzoyl-4-hydroxy-5-phenyl pyrazole,9) and β-penylpropiophenone,10) and two other unidentified oils were also obtained. The yield of the pyrazole derivative increases in proportion to the concentration of diazoketone, accompanied by a decrease in the nitrogen evolved. A detailed report on this point will be published in the near future.

Results and Discussion

With all the diazoketones and solvents studied, the evolution of nitrogen followed the first-order equation roughly, with different degrees of accuracy. A short induction period was observed at about a 10—15 percent completion of the reaction; pseudo-first-order rate constants were calculated according to Eq. (1) in a manner which has been described previously:6)

$$k\times t = 2.303 \times \log (V_\infty/(V_\infty - V_t)) \qquad (1)$$

where the reaction time, t, is taken from the apparent end of the induction period, and where V_∞ indicates the total volume of nitrogen and V_t, the volume of nitrogen at time t.

In *t*-butyl alcohol, the reaction rates were examined at 30.0±0.01°C; the deposition of metallic silver was observed on the wall of the reaction vessel after a reaction was over, but the reaction medium was kept homogeneous during the kinetic measurement. In the 10—60% region of the reaction, the first-order equation (1) was applicable with an accuracy of about ±2%; thereafter, deviation from the first-order equation occurred. A typical example is shown in Fig. 1. The usual accuracy of the rate constant was a few percent points for each measurement, but the reproducibility was slightly lower. Particularly, the reproducibility for *p*-nitro-, *p*-chloro-, and *p*-bromo-α-diazoacetophenones appeared worse, probably because of their low solubility in *t*-butyl alcohol.

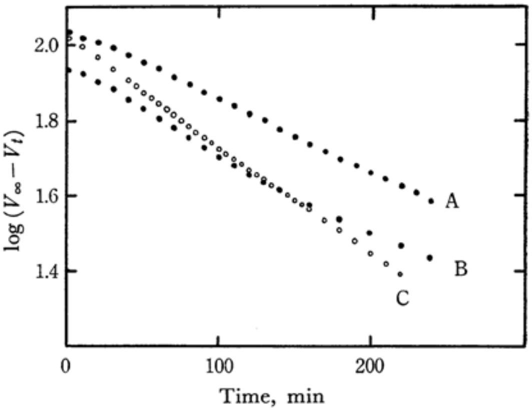

Fig. 1. The typical first-order plots for the Wolff rearrangement of substituted α-diazoacetophenones in *t*-butyl alcohol at 30.0°C.
A: p-C_2H_5O, B: p-Cl, C: H

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9) D. G. Farnum and P. Yates, *J. Am. Chem. Soc.*, **84**, 1399 (1962).

10) G. S. Fonken and W. S. Johnson, *ibid.*, **74**, 831 (1952).

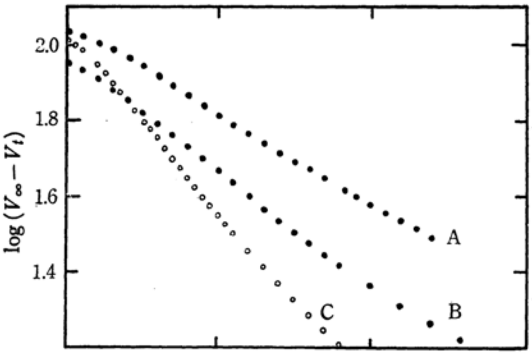

Fig. 2. The typical first-order plots for the Wolff rearrangement of substituted α-diazoacetophenones in isopropyl alcohol at 20.0°C.
A: p-C_2H_5O, B: p-Cl, C: H

TABLE 2. THE RATE CONSTANTS OF THE WOLFF REARRANGEMENT OF α-DIAZOACETOPHENONES IN t-BUTYL ALCOHOL AT 30.0°C, AND IN ISOPROPYL ALCOHOL AT 20.0°C*

Substituent	$k\times10^4$, min^{-1}	
	t-Butyl alcohol	Isopropyl alcohol
p-CH_3O	34.0 ± 0.8	50.6 ± 0.9
p-C_2H_5O	46.1 ± 1.8	57.4 ± 0.6
p-t-C_4H_9		134.0 ± 2.0
H	71.1 ± 0.8	114.0 ± 3.0
p-Cl	57.1 ± 0.8	66.8 ± 3.8
p-Br	66.5 ± 4.5	68.0 ± 2.8
m-Br		108.0 ± 0.3
p-NO_2	70.3 ± 5.0	75.0 ± 6.0
m-CH_3	71.5 ± 0.7	

* The reaction condition used was as follows: diazoketones, 5.0 mmol; silver benzoate, 0.100 g (0.44 mmol); triethylamine, 2.0 ml; solvent, 100 ml.

In these cases the total volume of nitrogen evolved was only 80—85% of the theoretical yield, while quantitative amounts of nitrogen were evolved from other diazoketones. The first-order rate constants of the Wolff rearrangement in t-butyl alcohol are given in Table 2. In isopropyl alcohol, which has a higher solubility to diazoketones than does t-butyl alcohol, the reaction rates were measured at 20.0±0.01°C, and the first-order equation was adopted until about 70% completion of the reaction with fairly good reproducibility as is shown in Table 2. A typical first-order relationship is shown in Fig. 2. The solubility of diazoketones was considerably increased by mixing a toluene to t-butyl alcohol, and the linearity of the $\log(V_\infty - V_t)$ $vs.$ time curve was also observed. The first-order rate constants at 30.0±0.01°C are given in Table 3.

Homogeneous reaction conditions were also

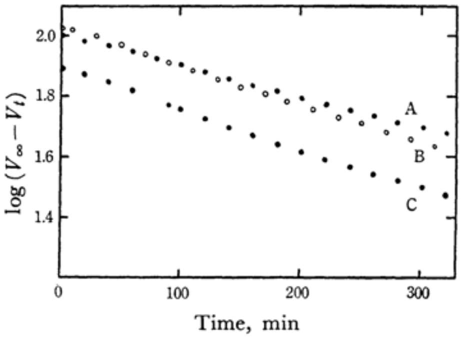

Fig. 3. The typical first-order plots in a mixed solvent of t-butyl alcohol and toluene at 30.0°C.
A: p-CH_3O, B: H, C: p-Br

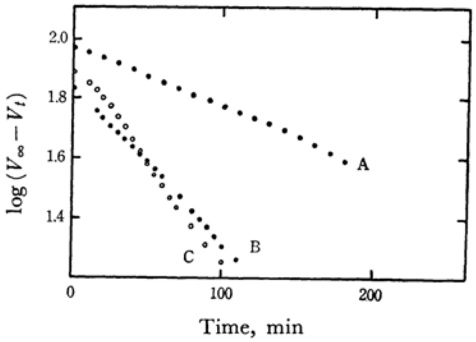

Fig. 4. The typical first-order plots of the catalytic decomposition of diazoketones in toluene at 40.0°C.
A: p-C_2H_5O B: p-Cl C: H

TABLE 3. THE RATE CONSTANTS OF THE WOLFF REARRANGEMENT OF α-DIAZOACETOPHENONES IN THE MIXED SOLVENT OF t-BUTYL ALCOHOL AND TOLUENE AT 30.0°C, AND THE DECOMPOSITION RATE[a)] CONSTANTS IN TOLUENE AT 40.0°C

Substituent	t-Butyl alcohol-toluene[b)]	Toluene	
	$k\times10^4$, min^{-1}	$k\times10^4$, min^{-1}	N_2, %
p-CH_3O	21.4 ± 1.5	56.6 ± 1.2	93
p-C_2H_5O	29.3 ± 3.0	44.4 ± 1.1	88
p-t-C_4H_9	36.6 ± 1.1	173.0 ± 11.0	83
p-CH_3	36.3 ± 3.3	103.0 ± 4.0	92
H	31.8 ± 1.6	174.0 ± 7.0	88
p-C_6H_5	35.0 ± 4.0	205.0 ± 6.0	73
p-Cl	32.1 ± 2.0	110.0 ± 9.0	68
p-Br	32.6 ± 0.6	103.0 ± 9.0	68
m-NO_2	31.3 ± 1.5	61.9 ± 9.0	67
p-NO_2	50.3 ± 1.9	74.8 ± 1.4	67
m-Br		113.0 ± 11.0	67

a) Kinetic measurement was carried out under the following condition:
diazoketones, 5.0 mmol; silver benzoate, 0.100 g (0.44 mmol); triethylamine, 2.0 ml; solvent, 100 ml.

b) The ratio of t-butyl alcohol and toluene was 1 : 3 in volume.

attained when toluene was used as the solvent. The accuracy of the first-order rate constants obtained was somewhat lower than that in other solvents, and the reproducibility was also lower (Fig. 4). The rate constants obtained at 40.0±0.01°C are listed in Table 3.

As has been shown above, the smaller substituent effect with quite a large experimental uncertainty makes for a difficulty in the detailed analysis of the data. However, it is apparent that the strongly electron-releasing conjugative substituents at the para-position, such as methoxy and ethoxy group, significantly retard the reaction. Without these groups, approximately linear Hammett plots are obtained in all cases, with small negative ρ-values (Figs. 5—8).[11] The gross pattern of the plots appears to be the same for the substituent effects obtained in various solvents. A similar Hammett relation was obtained in the Curtius rearrangement of meta- and para-substituted benzazides in the usual solvents.[7] The molecular structure of α-diazoacetophenone and benzazide are isoelectronic, and the mechanism of both rearrangements may be expected to be analogous. The similar substituent effects suggest a similarity in the transition states of the two rearrangements. As has been mentioned earlier, the molecular structure of the transition state of the Curtius rearrangement closely resembles that of the ground-state, because the benzazide molecule is of a comparatively high energy and gives an extremely stable nitrogen molecule, with the liberation of a large heat of formation. This might be reflected in the small polar substituent effects and in the relatively large retarding effect due to the resonance stability of the ground-state molecules. The situation should be much the same for the present reaction.

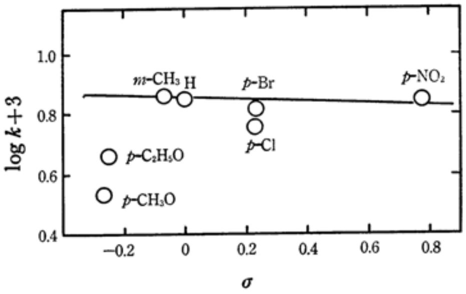

Fig. 5. Plots of reaction rates of substituted α-diazoacetophenones in t-butyl alcohol at 30.0°C against Hammett σ.

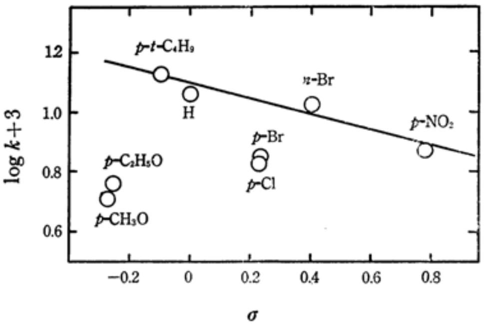

Fig. 6. Hammett plots (in isopropyl alcohol at 20.0°C).

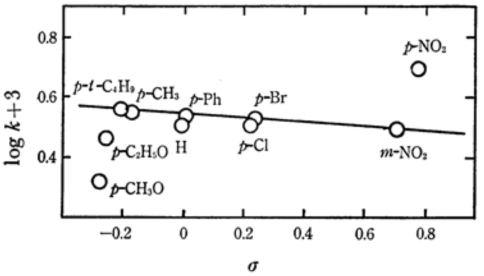

Fig. 7. Hammett plots (in a mixed solvent of t-butyl alcohol and toluene at 30.0°C).

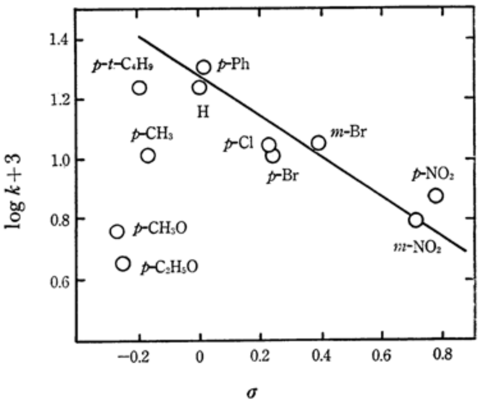

Fig. 8. Hammett plots of the decomposition of substituted α-diazoacetophenones in toluene at 40.0°C.

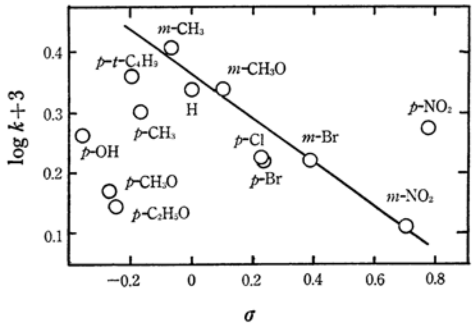

Fig. 9. Hammett plots for the reaction of Curtius rearrangement of substituted benzazides in toluene.

In a previous paper[6] we proposed the following reaction mechanism for the Wolff rearrangement in an alcoholic solution catalyzed by silver benzoate-triethylamine:

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[11] Jaffe's σ-values were used. H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

$$\underset{\text{(I)}}{\mathrm{RCOCHN_2}} + (\mathrm{C_2H_5})_3\mathrm{N} \rightarrow \underset{\text{(II)}}{[\mathrm{RCO\ddot{C}{=}N_2}]^{\ominus}} + (\mathrm{C_2H_5})_3\overset{\oplus}{\mathrm{N}}\mathrm{H} \qquad (2)$$

$$\underset{\text{(II)}}{[\mathrm{RCO\ddot{C}{=}N_2}]^{\ominus}} + [\mathrm{AgN(C_2H_5)_3}]^{\oplus} \rightarrow \underset{\text{(III)}}{[\mathrm{RCO\ddot{C}{=}}\overset{\ominus}{\mathrm{N}}_2\text{—}\overset{\oplus}{\mathrm{Ag}}\mathrm{N(C_2H_5)_3}]} \qquad (3)$$

$$\underset{\text{(III)}}{[\mathrm{RCO\ddot{C}{=}}\overset{\ominus}{\mathrm{N}}_2\text{—}\overset{\oplus}{\mathrm{Ag}}\mathrm{N(C_2H_5)_3}]} \rightarrow \underset{\text{(IV)}}{[\mathrm{RCO}\underset{\cdot\cdot}{\overset{\cdot\cdot\,\ominus}{\mathrm{C}}}\text{—}\overset{\oplus}{\mathrm{Ag}}\mathrm{N(C_2H_5)_3}]} + \mathrm{N_2} \qquad (4)$$

$$\underset{\text{(IV)}}{[\mathrm{RCO}\underset{\cdot\cdot}{\overset{\cdot\cdot\,\ominus}{\mathrm{C}}}\text{—}\overset{\oplus}{\mathrm{Ag}}\mathrm{N(C_2H_5)_3}]} \rightarrow \underset{\text{(V)}}{[\mathrm{R\text{-}\ddot{C}{=}C{=}O}]^{\ominus}} + [\mathrm{AgN(C_2H_5)_3}]^{\oplus} \qquad (5)$$

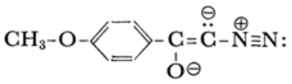
$$\underset{\text{(V)}}{[\mathrm{R\text{-}\ddot{C}{=}C{=}O}]^{\ominus}} + \mathrm{BH} \rightarrow \underset{\text{(VI)}}{\mathrm{RCH{=}C{=}O}} + \mathrm{B}^{\ominus} \qquad (6)$$

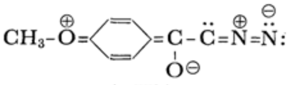
$$\underset{\text{(VI)}}{\mathrm{RCH{=}C{=}O}} + \mathrm{R'OH} \rightarrow \mathrm{RCH_2COOR'} \qquad (7)$$

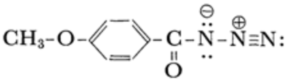
$$\underset{\text{(III)}}{[\mathrm{RCO\ddot{C}{=}}\overset{\ominus}{\mathrm{N}}_2\text{—}\overset{\oplus}{\mathrm{Ag}}\mathrm{N(C_2H_5)_3}]} \rightarrow \underset{\text{(V)}}{[\mathrm{R\text{-}\ddot{C}{=}C{=}O}]^{\ominus}} + \mathrm{N_2} + [\mathrm{AgN(C_2H_5)_3}]^{\oplus} \qquad (8)$$

BH: $(\mathrm{C_2H_5})_3\overset{\oplus}{\mathrm{N}}\mathrm{H}$, $\mathrm{RCOCHN_2}$, $\mathrm{R'OH}$, *etc.*

In this scheme, the rate-determining step is thought to be Eq. (4).⁶⁾ Therefore, the stability of the complex III, which corresponds to the ground state, will affect the reaction rate. The resonance contribution of VIIb*2 in *p*-methoxy-α-diazoacetophenone increases the double-bond character of the carbon-nitrogen bond, which is breaking in the transition state, and consequently decreases the reaction rate in the same manner in VIII as the Curtius rearrangement (Bond-energy Effect).⁷⁾


(VIIa)


(VIIb)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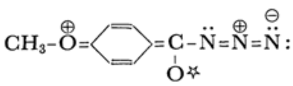
(VIIIb)

As has been described in the Experimental section, the reaction products of the decomposition of α-diazoacetophenone in a toluene solution*3 are entirely different from those of normal Wolff rearrangements in alcoholic solutions. The same mechanism seems to be applicable at least to the process of initial ketene formation in both reactions, because of the similarity in substituent effects.

The application of the Yukawa-Tsuno equation to the reaction rates in toluene shows quite a good linearity except for the *p*-phenyl group, as is shown in Fig. 10:

$$\log k/k_0 = -0.45(\sigma - 2.7\Delta\sigma_{\mathrm{R}}^{+}) - 0.05$$

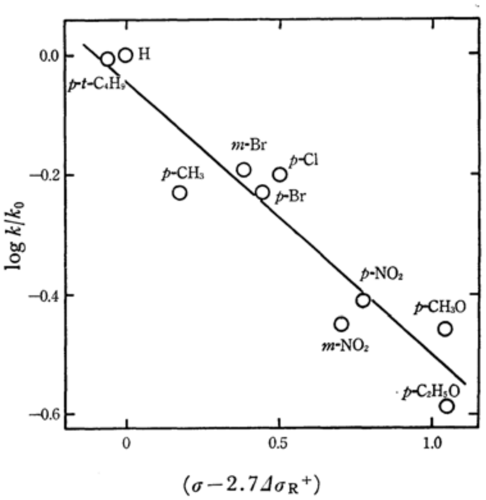

Fig. 10. Application of Yukawa-Tsuno equation for reaction rates in toluene at 40.0°C.

Similar correlation were also obtained for the substituent effect in the other solvents. Furthermore, the substituent effects on the Curtius rearrangement result in a rather good correlation:¹²⁾

$$\log k/k_0 = -0.30(\sigma^{\circ} - 1.04\Delta\bar{\sigma}_{\mathrm{R}}^{+})$$

Characteristic of these results is that, in all cases, large negative *r*-values are obtained. Generally a positive *r*-value should be obtained when a transition state is stabilized by an additional resonance between a positively-charged reaction

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*2 In VIIa and VIIb, the silver ion, having interaction with diazoketone-anion (III), is omitted for the sake of simplicity.

*3 Although a ketene reacts with alcohols to give esters in an alcoholic medium (Eq. (7)), a ketene is accumulated in the toluene solution and then reacts with the unreacted dizaoketone to give the pyrazole derivative and β-phenylpropiophenone. It is probably because of the accumulation of ketene that deviation from first-order equation occurs in the middle stage of a reaction in toluene.

12) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 873 (1965).

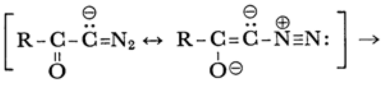
center and electron-releasing substituents.[13] On the contrary, a negative r-value, as observed in the present reaction, is possibly caused by a resonance stabilization in the ground-state species (III).

From the present data it is not apparent whether the elimination of nitrogen and the migration of the alkyl group proceed successively in two steps (Eqs. (4) and (5)) or in a concerted process in one step (Eq. (8)). The choice between one-step or two-step mechanisms has also not been made for the Curtius rearrangement; *i. e.*, Cram,[14] Horner,[15] and Lwowski[16] proposed a concerted mechanism, whereas Roberts[17] proposed a two-step mechanism, in which a nitrene intermediate was involved. The rate-determining step in both rearrangement is the process of nitrogen elimination. However, the bond-energy effect and polar effect observed in the Wolff rearrangement of substituted α-diazoacetophenones could provide no definite evidence suggesting either of the above mechanisms.

In order to clarify the problem, the kinetic isotope effect on the rearrangement of carbonyl-^{14}C and phenyl-1-^{14}C labeled α-diazoacetophenones was studied, measuring the radioactivity of the barium carbonate derived from the recovered α-diazoacetophenone. No apparent kinetic isotope effect was observed in either case within the range of experimental error. This result suggests the preference of a two-step mechanism over a concerted one; the phenyl-carbonyl bond should not be under breaking at the transition state. On the other hand, a positive isotope effect on the Curtius rearrangement of carbonyl-^{14}C, phenyl-1-^{14}C, and ^{15}N labeled benzazide has been observed by Fry;[18] for this reaction, a concerted mechanism mitght perhaps be suggested.

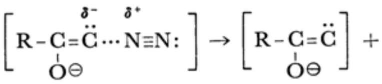
When a two-step mechanism is accepted for the Wolff rearrangement, the following two types of cleavage should be possible for the transition state of nitrogen elimination:

Ionic cleavage



$$\left[\mathrm{R{-}\underset{\overset{\Vert}{O}}{C}{-}\overset{\ominus}{\ddot{C}}{=}N_2} \leftrightarrow \mathrm{R{-}\underset{\overset{|}{O^{\ominus}}}{C}{=}\overset{\ominus}{\ddot{C}}{-}\overset{\oplus}{N}{\equiv}N{:}}\right] \rightarrow$$

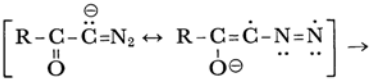
(III)



$$\left[\mathrm{R{-}\underset{\overset{|}{O^{\ominus}}}{C}{=}\overset{\delta^-}{\ddot{C}}\cdots\overset{\delta^+}{N}{\equiv}N{:}}\right] \rightarrow \left[\mathrm{R{-}\underset{\overset{|}{O^{\ominus}}}{C}{=}\ddot{C}}\right] + \mathrm{N_2} \qquad (9)$$

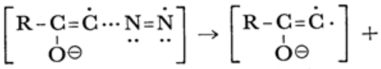
(IV)

Radical cleavage



$$\left[\mathrm{R{-}\underset{\overset{\Vert}{O}}{C}{-}\overset{\ominus}{\ddot{C}}{=}N_2} \leftrightarrow \mathrm{R{-}\underset{\overset{|}{O^{\ominus}}}{C}{=}\dot{C}{-}\underset{\cdot\cdot}{N}{=}\underset{\cdot\cdot}{\dot{N}}}\right] \rightarrow$$

(III)



$$\left[\mathrm{R{-}\underset{\overset{|}{O^{\ominus}}}{C}{=}\dot{C}\cdots\underset{\cdot\cdot}{N}{=}\underset{\cdot\cdot}{\dot{N}}}\right] \rightarrow \left[\mathrm{R{-}\underset{\overset{|}{O^{\ominus}}}{C}{=}\dot{C}\cdot}\right] + \mathrm{N_2} \qquad (10)$$

(IV)

Since radical and ionic cleavages, having the same reaction origin (III)*2 and reaction terminus (IV),*2 are different only in the electronic structures of the transition state (or the intermediate), it will be difficult to distinguish these two mechanisms strictly. The possibility of a radical-cleavage mechanisms can not be denied because of their small ρ-values, but an apparently negative ρ-value was still given for the reaction in toluene. The smaller effect of substituents in alcoholic solutions may indicate a less significant polarization of the transition state, even if the cleavage may proceed through the ionic mechanism.

The Yukawa-Tsuno equation has been reported to be applicable to radical reactions also. For example, the decomposition of substituted phenylazo triphenylmethane,[19] giving negative ρ- and r-values:

$$\log k/k_0 = -0.92(\sigma - 0.9\Delta\sigma_{\mathrm{R}}{}^+)$$

It is of interest to note that these substituent effects are quite different from the results of the photochemical Wolff rearrangement reported by Ziffer.[20] They showed that the Hammett relationship gave a straight line with respect to the quantum yield of substituted α-diazoacetophenones in ethanol, but correlation was not so good. Foffani[21] reported that a linear Hammett relationship with respect to quantum yield of α-diazoacetophenones was not obtained in methanol, n-hexane, and ethyl acetate. Therefore, some problems seem to remain in the phtochemical Wolff rearrangement.

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