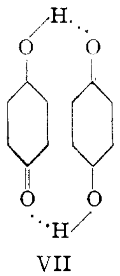
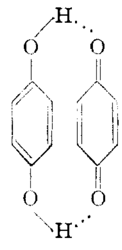
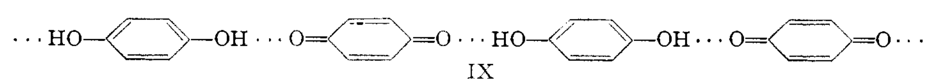


VII



VIII



IX

with the results reported by Gragerov and Miklukhin[2] and here.

Formula VIII, proposed by Michaelis, permits each moiety to retain its identity when the complex is decomposed. The deep color of the quinhydrone complexes may better be explained on the basis of this formula than of formula IX, since the highly polarizable hydroquinone ring is acted upon at close range by the positive charge centered in the quinone ring. A parallel case may be cited in naphacene picrate, which is red. The strong dipole–dipole interaction implied by this formulation would help to stabilize the complex.

Formula IX has been proposed by Palacios and Foz[13] on the basis of X-ray diffraction patterns from solid quinhydrone. The complex is held together by hydrogen bonding alone, and it is difficult to account for the development of an intense color. Evidence supporting this formula is available in the paper of Wagner and Grunewald[14] reporting measurements of light absorption due to complex formation in moderately concentrated quinone–hydroquinone solutions. Their results indicated that there were deviations from the simple mass action law in the direction implying formation of complexes containing more than two components.

The findings of Davies[15] anent the infrared absorption spectrum of quinhydrone, and of Coryell,[16] Palacios and Foz,[13] and Sunder Lal and Nur-ul-Haq Khan[17] on the diamagnetism of the complex fit equally well with formulas VIII and IX.

Gragerov and Miklukhin[2] have stated that the hydrogen bonds in quinhydrone are not stabilized by resonance of the type

$$=\!O\cdots H{-}O{-} \longleftrightarrow {-}O{-}H\cdots O\!=$$

since the easy transfer of a proton pair would, contrary to findings, convert a quinone to a hydroquinone nucleus. They have neglected the fact that transfer of an electron pair is also necessary, and that the two hydrogen bonded atoms are not connected by a conducting network of bonds, as they are in such classical cases as *o*-nitrophenol or salicylaldehyde. Thus non-exchange in the quinhydrone complex cannot be rigorously interpreted as refuting or supporting the statement that both forms contribute to a resonance hybrid structure in quinhydrones.

(13) Palacios and Foz, *Anal. Fis. Quim.*, **34**, 779 (1936).

(14) C. Wagner and K. Grunewald, *Z. Elektrochem.*, **46**, 265 (1940).

(15) M. M. Davies, *J. Chem. Phys.*, **8**, 557 (1940).

(16) C. D. Coryell, as quoted in Pauling, "Nature of Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 278.

(17) Sunder Lal and Nur-ul-Haq Khan, *Current Sci.*, **13**, 312 (1944).

UPTON, L. I., N. Y. RECEIVED APRIL 7, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Reactions of Diazoketones. IV. Kinetics of the Decomposition of Some *p*-Substituted-α-diazoacetophenones in Acetic Acid[1]

BY JOHN F. LANE AND ROBERT L. FELLER[2]

The rates of decomposition of five *p*-substituted-α-diazoacetophenones in acetic acid have been studied under a variety of conditions and have been found to be of the first order with respect to diazoketone. The logarithms of the rates at 40° and 60°, plotted against appropriate values of Hammett's parameter σ, give straight lines of negative slope (ρ). The rate of decomposition of *p*-nitro-α-diazoacetophenone is slightly decreased by addition of sodium acetate. Addition of lithium chloride, however, causes a rapid reaction, leading to the formation of *p*-nitrophenacyl chloride, the kinetics of which are of the first order in diazoketone and in chloride ion. These results are discussed in terms of a mechanism involving preliminary reversible proton transfer from solvent to diazoketone followed by bimolecular reaction between the diazonium ion so produced and the acetate (or chloride) ion.

The aliphatic diazoketones, $RCOCHN_2$, which are readily obtained[3] by interaction of acyl chlorides with diazomethane, undergo two reactions of considerable synthetic interest

$$RCOCHN_2 + HB \longrightarrow RCH_2COB + N_2 \; (B = OAlk, OH, NH_2, NHR') \quad (1)$$

$$RCOCHN_2 + HA \longrightarrow RCOCH_2A + N_2 \; (A = OAlk, OH, O_2CR', Hal) \quad (2)$$

The first of these, known as Wolff's rearrangement,[4] occurs in slightly basic media and is frequently aided by traces of colloidal metals such as silver; the second occurs in acidic media and serves as a convenient path to the α-ketols, $RCOCH_2OH$,

(1) For detailed material supplementary to this article order Document 3296 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images one inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) The Mellon Institute, Pittsburgh, Penna.

(3) (a) F. Arndt, *et alii*, *Ber.*, **60**, 1364 (1927); **61**, 1122, 1949 (1928); (b) W. Bradley and R. Robinson, *J. Chem. Soc.*, 1310 (1928); (c) W. Bradley and G. Schwarzenbach, *ibid.*, 2904 (1928).

(4) L. Wolff, *Ann.*, **394**, 25 (1912). *Cf.* R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1942, Volume I, Chapter 2.

and their derivatives. Earlier papers[5] of this series were concerned exclusively with examples of reaction (1) involving optically active groups R. The present investigation, on the other hand, concerns itself with examples of reaction (2) so chosen as to provide the basis for a quantitative relationship between the structure of R and the reactivity of the corresponding diazoketone toward acetic acid.

Experimental

Materials.—Acetic acid, b.p. 117.9–118.1° (760 mm.), was prepared from the commercial acid as recommended by Weissberger and Proskauer.[6] Analysis for water[7] showed a water content of 0.15 ± 0.02%. The diazoketones used in these experiments were prepared by the method of Wilds and Meader.[8] All, except *p*-bromo-α-diazoacetophenone, were known compounds. This substance was obtained in nearly quantitative yield by the interaction of *p*-bromobenzoyl chloride with an excess of diazomethane in ethereal solution. Recrystallized from dioxane it melted at 123.5–124.5°.[9]

Anal. Calcd. for $C_8H_5N_2Br$: C, 42.69; H, 2.24; N, 12.4. Found[10]: C, 42.51; H, 2.52; N, 12.3.

Treatment of the compound, dissolved in a small amount of dioxane, with cold concentrated hydrobromic acid converted it readily to *p*-bromophenacyl bromide, m.p. 110–111°, reported[11] 109.7°.

The melting points of the other *p*-substituted-α-diazoacetophenones were: *p*-NO_2, 116–117° (reported[3] 116–117°); *p*-Cl, 115–116° (reported[6] 113–114°); *p*-H, 48–49° (reported[4] 49–50°); *p*-CH_3, 49–51° (reported[8] 48–51°).

Kinetic Measurements.—The apparatus used in the kinetic studies consisted of a water-jacketed gas buret of 100 ml. capacity attached through a capillary tube of 1-mm. bore to a similarly jacketed condenser, fitted at the bottom with a 24/40 ₸ inner joint. Reaction vessels of 500-ml. capacity (either flat or round-bottomed), equipped with 24/40 ₸ outer joints, were affixed to the condenser by means of wooden clamps. The entire apparatus was clamped to a moveable frame to facilitate lowering of the reaction vessel into a bath, the temperature of which was maintained constant within a precision of ±0.01°. Stirring was effected by means of a magnetic stirrer (A. H. Thomas Co., Philadelphia) placed beneath the bath directly below the reaction vessel.

In general 50 ml. of acetic acid was transferred with the aid of a pipet from a stock bottle to the reaction flask, which was then sealed with a calcium chloride tube and immersed in the bath until thermal equilibrium was reached (15 to 20 minutes). A known amount (3 to 6 mmoles) of diazoketone was then rapidly introduced, the flask joined to the condenser and the stirrer started. This point was taken as zero time. For the first period (10 to 20 minutes) of reaction the apparatus was left open through a stopcock to permit the escape of expanding vapors. After thermal equilibrium had been established, the stopcock was closed, and readings were taken in the gas buret (water, saturated with nitrogen, being used as the leveling fluid) until the reaction was complete to the extent of at least 75% (usually 90%). During the period of measurement the stirrer was ordinarily rotated at speeds of 100 to 150 r.p.m., although great variation in the speed of stirring was found (Table I) to have little effect on the results. For each reaction vessel used the volume of free air space (600 to 650 ml.) was determined to the entry point into the gas buret. Volume readings could then be corrected for fluctuations in the external pressure. Usually this correction was made to the mean pressure obtaining during the run. From the increments of time and volume so obtained it was then possible to calculate, by the method outlined below, a satisfactory value for the specific rate of decomposition of the diazoketone.

Products of the Reaction of the Diazoketones with Acetic Acid.—To investigate the extent of the desired reactions samples of the diazoketones were dissolved in acetic acid and the solutions allowed to remain at 60° until no further evolution of nitrogen occurred. The solvent was then removed *in vacuo*. In each case the residues were sharply melting, crystalline substances, corresponding in weight to 96–98% of the expected yield of *p*-substituted phenacyl acetate. Recrystallization from ethanol raised the melting points by about 1–2°.

MELTING POINTS AND ANALYSES FOR ACETOXYL

Formula	M.p., °C.	OAc, % Calcd.	Found[10]
$C_{10}H_9O_5N$	123.5–124.5	26.5	26.9
$C_{10}H_9O_3Br$	85 – 86	23.0	23.3
$C_{10}H_9O_3Cl$	70.5– 71.5	27.8	28.4
$C_{10}H_{10}O_3$	47.5– 48	33.1	33.4
$C_{11}H_{12}O_3$	84.5– 85	30.7	30.9

Reaction of *p*-Nitro-α-diazoacetophenone with Lithium Chloride.—To a solution of 0.2120 g. (0.00500 mole) of lithium chloride in 50.0 ml. of acetic acid at 40.05° was added 0.9555 g. (0.00500 mole) of *p*-nitro-α-diazoacetophenone, the reaction vessel immediately attached to the apparatus and the stirrer started. After 20 minutes the stopcock was closed and the following readings obtained:

Time, min.	Volume (V) 13°/758.5 mm.
20.0	610.0
25.0	613.9
30.0	616.8
40.0	621.1
50.0	624.3
66.0	627.9
90.0	631.3
150.0	644.7 ($V'\infty$)

Since the theoretical value of $V\infty$ under these conditions is 119 ml., the volume of nitrogen collected represents only the last 30% of the reaction and decomposition to the extent of 70% must have occurred in the first twenty minutes. Figure 1 shows a plot of the data in which time is plotted against the reciprocal of $V'\infty - V$. The slope of the straight line, obtained by the method of least squares, is 6.55×10^{-4} which represents a bimolecular constant having the value $k_2 = 0.780$ l. mole^{-1} min.$^{-1}$.

Evaporation of the solvent gave 95.6% of the theoretical amount of *p*-nitrophenacyl chloride, m.p. 89–90°. A sample recrystallized from ethanol melted at 90–91° and gave no depression of m.p. when mixed with another preparation, m.p. 90–91°, which had been obtained by the action of concentrated hydrochloric acid on the diazoketone.

Anal. Calcd. for $C_8H_6O_3NCl$: Cl, 17.8: Found[10]: Cl, 18.0.

Treatment of Experimental Data

The reactions of diazoacetic ester[12] and of diphenyl diazomethane[13] with carboxylic acids have been found to be first-order with respect to the diazo compounds. Hence, the reactions of the diazoketones with acetic acid were expected to

---

[5] Three papers on the Wolff rearrangement, J. F. Lane, J. Willenz, A. Weissberger and E. S. Wallis, *J. Org. Chem.*, **5**, 276 (1940); J. F. Lane and E. S. Wallis, *ibid.*, **6**, 443 (1941); J. F. Lane and E. S. Wallis, THIS JOURNAL, **63**, 1674 (1941), are considered Parts I, II and III, respectively, of the series.

[6] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford University Press, Clarendon, 1935, p. 62.

[7] G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem.*, *Anal Ed.*, **15**, 272 (1943).

[8] A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

[9] All melting points reported in this paper were determined on the Kofler micro hot-stage.

[10] Microanalysis by Mr. J. Alicino, Squibb Institute for Medical Research, New Brunswick, New Jersey.

[11] W. L. Judefind and E. E. Reid, THIS JOURNAL, **42**, 1043 (1920).

[12] (a) *Cf.* L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940 pp. 288–289; (b) A. Weissberger and J. Hogen, *Z. physik. Chem.*, **A156**, 321 (1931).

[13] J. D. Roberts, *et alii*, THIS JOURNAL, **71**, 2923 (1949); **72**, 628 (1950); Abstracts, 116th Meeting of the American Chemical Society, Atlantic City, N. J., 1949, p. 69 M.

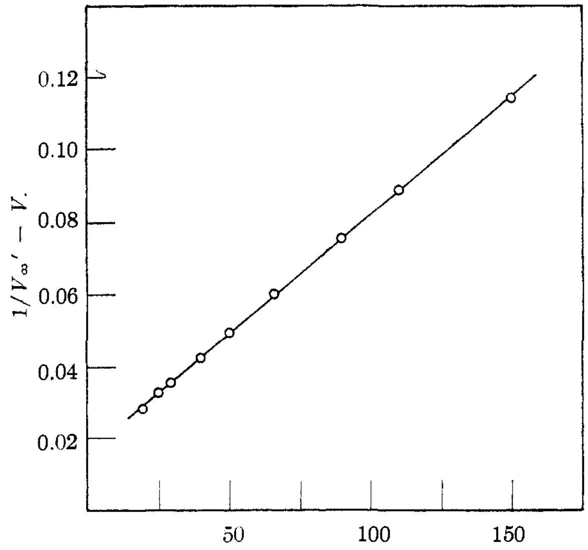


Fig. 1.—Dependence of the evolution of nitrogen with time for the reaction of *p*-nitro-α-diazoacetophenone (0.1 *M*) with lithium chloride (0.1 *M*) in acetic acid at 40.0°.

follow a (pseudo) first-order law, since the activity of the acetic acid remains constant over the period of reaction. Although, theoretically, it would have been possible to ascertain this and to obtain values for the specific rate constants by inserting experimental data into the ordinary form of the first-order equation

$$k = (2.303/t) \log V_\infty/(V_\infty - V) \qquad (3)$$

where V_∞ is the total volume of nitrogen evolved in infinite time and V, the volume at time t, actually the direct determination of V_∞ proved so difficult and tedious that recourse was made to a graphical method of analyzing the data which effectively by-passed this difficulty.

In the general first-order reaction

$$A \longrightarrow B + C + \cdots$$

if x denote the concentration of an experimentally determinable product B, the differential equation for its production is

$$\dot{x} = k(a - x) \qquad (4)$$

where a is the initial concentration of A (or the infinity value of x). The solution of (4) is

$$x = a(1 - e^{-kt}) \qquad (5)$$

Substitution of (5) into (4) gives

$$\dot{x} = kae^{-kt} \qquad (6)$$

or, expressed logarithmically

$$\log \dot{x} = \log ka - kt/2.303 \qquad (7)$$

While in practice $\dot{x}$ is difficult to determine precisely, it may, as shown below, be replaced without appreciable error in this equation by the average change in x over a short period of time, $\bar{\dot{x}} = (x_2 - x_1)/(t_2 - t_1) = \Delta x/\Delta t$. So modified equation (7) becomes

$$\log \bar{\dot{x}} = \log ka - k\bar{t}/2.303 \qquad (8)$$

where $\bar{t}$ is the mean time, $(t_2 + t_1)/2$, between two measurements and $\bar{\dot{x}}$ has replaced the instantaneous value, $(\dot{x})_{\bar{t}}$, of the derivative at $\bar{t}$. If, now, experimentally determined values of $\log \bar{\dot{x}}$ are plotted against corresponding values of $\bar{t}$, straight lines are obtained, the slopes of which (determined by the method of least squares) are $k/2.303$ and the intercepts of which at zero time are the quantities log *ka*. Thus, a simultaneous determination of k and of a becomes possible.

So long as the values of Δt do not exceed about one-half of the half-life of the reaction ($\tau = (2.303 \log 2)/k$) the error introduced by identifying $\bar{\dot{x}}$ with $(\dot{x})_{\bar{t}}$ is less than 1%. This may easily be demonstrated as follows. Let the error so introduced be equal to or greater than 1%. Then

$$[\bar{\dot{x}} - (\dot{x})_{\bar{t}}]/(\dot{x})_{\bar{t}} \geq 0.01 \qquad (9)$$

or

$$\Delta x/\Delta t(\dot{x})_{\bar{t}} \geq 1.01 \qquad (10)$$

With the aid of (5) and (6) equation (10) may be re-expressed in the form

$$(e^{k\Delta t/2} - e^{-k\Delta t/2})/k\Delta t \geq 1.01 \qquad (11)$$

If γ be defined as that fraction of τ represented by Δt, then (11) becomes

$$(e^{0.693\gamma/2} - e^{-0.693\gamma/2})/0.693\gamma \geq 1.01 \qquad (12)^{1}$$

But this condition obtains only when $\gamma \geq 0.48$ or when Δt, as stated above, exceeds about one-half of the value of τ.

In specific applications to the problem at hand equation (8) was applied in the form

$$\log \Delta V/\Delta t = \log kV_\infty - k\bar{t}/2.303 \qquad (15)^{1}$$

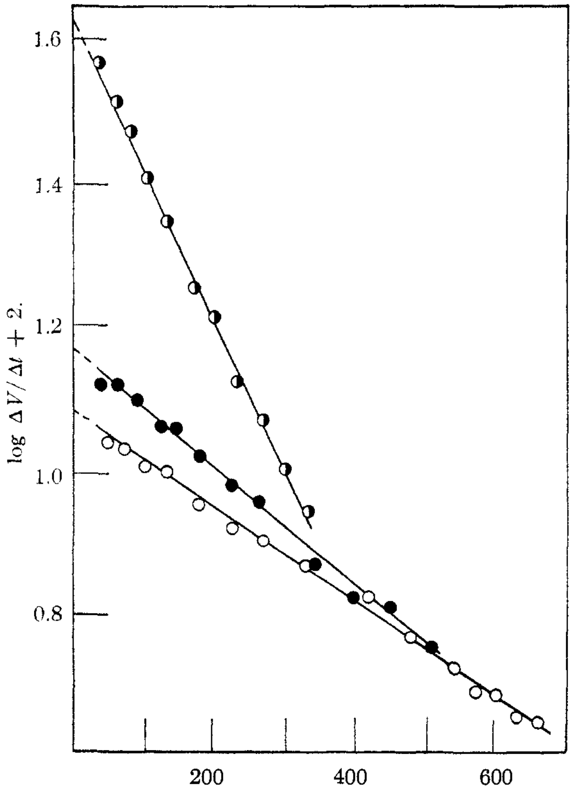


Fig. 2.—A plot (according to Equation 15) of the data given in Table IV[1]: ◑, *p*-methyl-α-diazoacetophenone at 40.05; ●, *p*-bromo-α-diazoacetophenone at 40.05°; ○, *p*-nitro-α-diazoacetophenone at 50.10°.

TABLE I

RATES OF DECOMPOSITION OF *p*-NITRO-α-DIAZOACETOPHENONE IN ACETIC ACID UNDER VARIOUS CONDITIONS

Temperature →	50.10°		60.30°		70.60°		80.00°	
	M^a	k_1^b	M	k_1	M	k_1	M	k_1
	0.059[c]	1.60	0.074	3.88	0.097	9.42	0.076	22.0
	.080[c]	1.61	.074	4.09	.084	9.60	.076	21.1
	.060	1.58	.075	4.08	.097	9.48	.083	20.4
	.090	1.63	.078	3.99			.066	20.2
	.076	1.56	.074[e]	3.73				
	.121[d]	1.62	.074[e]	3.96				
	.087[d]	1.61	.074[e]	3.57				
Mean $k_1^{b,f}$	1.60 ± 0.01		4.01 ± 0.04[g]	(3.75 ± 0.08[h])	9.50 ± 0.04		20.9 ± 0.3	

[a] Molarity of diazoketone. [b] 10^3 min.$^{-1}$. [c] Stirring speed *ca.* 200 r.p.m. [d] Stirring speed *ca.* 40 r.p.m. [e] 0.50 M in sodium acetate. [f] ±The probable error of the mean. [g] First four values. [h] Last three values.

Values of $\Delta V/\Delta t$ were chosen to give ΔV a value ranging from 5 to 15 ml. in order to minimize errors in the buret readings. Typical examples of the graphical treatment of data[1] are given in Fig. 2.

In Table I are given rate constants for the decomposition of *p*-nitro-α-diazoacetophenone under a variety of conditions. Table II presents data on the reactivities of the various diazoketones at 40° and 60°, and Table III gives the thermodynamic quantities of activation calculated from these data by means of Eyring's[14] equation for the temperature dependence of the specific rate

$$k = \frac{\mathbf{k}T}{\mathbf{h}} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (16)$$

Figure 3 shows graphically the linear dependence of log $k\mathbf{h}/\mathbf{k}T$ on $1/T$ for *p*-nitro-α-diazoacetophenone. In Fig. 4 the data of Table II, expressed logarithmically, are plotted against the appropriate values of Hammett's[15] parameter σ.

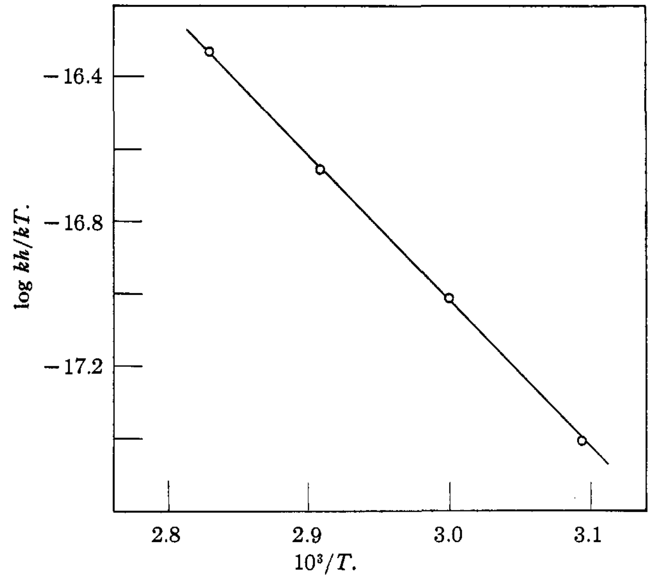


Fig. 3.—Temperature dependence of the reaction of *p*-nitro-α-diazoacetophenone with acetic acid according to the theory of absolute reaction rates (slope = − $\Delta H\ddagger/2.303\ R$).

Discussion

Extensive investigations on the acid-catalyzed decomposition of diazoacetic ester have led to the conclusion[12a] that in the water the first step is a reversible proton transfer

$$\mathrm{EtO_2CCHN_2 + H_3O^{\oplus} = EtO_2CCH_2N_2^{\oplus} + H_2O} \quad (17)^1$$

TABLE II

RATES OF DECOMPOSITION OF *p*-SUBSTITUTED-α-DIAZOACETOPHENONES IN ACETIC ACID AT 40° AND 60°

Substituent	k_1 (10^3 min.$^{-1}$) 40.05°	60.30°
NO_2	0.63 ± 0.02[a]	4.01 ± 0.04[b]
Br	1.95 ± 0.02[c]	11.8 ± 0.2[c]
Cl	1.98 ± 0.01[c]	12.0 ± 0.2[c]
H	2.94 ± 0.02[c]	19.2 ± 0.1[c]
CH_3	4.88 ± 0.05[c]	30.3 ± 0.3[d]

[a] Estimated graphically from Figure 3. [b] From Table I. [c] Two determinations. [d] Three determinations.

TABLE III

THERMODYNAMICS OF ACTIVATION FOR THE DECOMPOSITION OF *p*-SUBSTITUTED-α-DIAZOACETOPHENONES IN ACETIC ACID

Substituent	$\Delta F^{\ddagger}_{298}$ (kcal.)	$\Delta H^{\ddagger}$ (kcal.)	$\Delta S^{\ddagger}$ (e.u.)
NO_2	25.1	18.3	−23
Br	24.4	18.0	−22
Cl	24.4	18.0	−22
H	24.2	18.8	−18
CH_3	23.9	18.3	−19

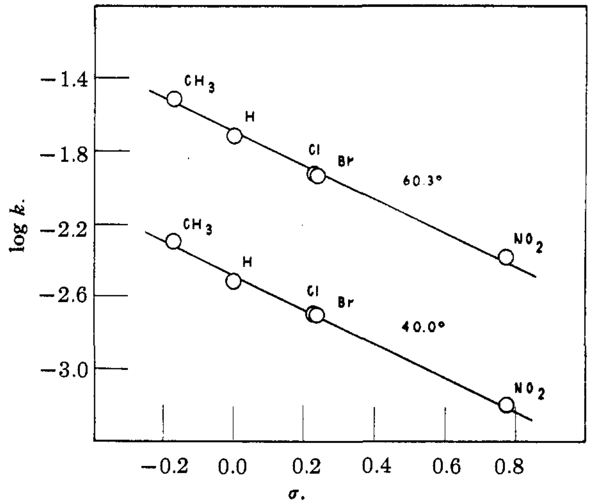


Fig. 4.—Dependence of the rates of decomposition in acetic acid of *p*-substituted-α-diazoacetophenones on Hammett's parameter σ at 40.0° (ρ = − 0.914, *r* = 0.027) and at 60.3° (ρ = −0.898, *r* = 0.024).

---

(14) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 196.

(15) Reference 12a, p. 188.

followed by a rate-determining bimolecular reaction of the diazonium ion so produced with water, or with anions such as nitrate or chloride, to give glycolic ester or one of its derivatives. In nonpolar solvents, such as benzene, reaction with carboxylic acids again involves a preliminary reversible proton transfer, followed by reaction of the diazonium ion with a second mole of acid.[12] Roberts[13] has recently reported that the reaction of diphenyldiazomethane with acids in alcohol shows a general acid catalysis and has suggested for this reaction a mechanism involving the initial production of a diazonium ion which, after loss of nitrogen to give the benzhydryl carbonium ion, is ultimately converted to benzhydryl ethyl ether.

In view of these findings it is not unreasonable to suppose that the initial stage of the reactions studied here consists in a reversible proton transfer between diazoketone and solvent

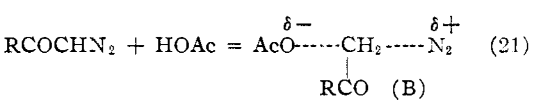
$$RCOCHN_2 + HOAc = \underset{(A)}{RCOCH_2N_2^{\oplus}} + OAc^{\ominus} \quad (19)$$

Several possibilities might be contemplated for the subsequent fate of the diazonium ion (A). Thus, it might undergo (a) bimolecular reaction with the solvent, (b) loss of nitrogen followed by reaction with the solvent of the carbonium ion so produced or (c) bimolecular reaction with the acetate ion

$$RCOCH_2N_2^{\oplus} + OAc^{\ominus} \longrightarrow RCOCH_2OAc + N_2 \quad (20)$$

We are inclined toward the third possibility for two reasons. First, the addition of a relatively large amount of sodium acetate has only a slight effect (Table V[1]) on the rate of decomposition of *p*-nitro-α-diazoacetophenone in acetic acid at 60°. The mechanisms involving (a) and (b) above, however, would lead to the prediction that added acetate ions, by repressing reaction (19), should markedly decrease the rate of decomposition. Second, the rate of decomposition of the diazoketone is markedly enhanced by the addition of chloride ions, and in this case the kinetics are demonstrably bimolecular, which is in harmony with the possibility (c) where chloride has replaced acetate.

According to this interpretation the over-all process of activation to which the thermodynamic quantities of Table VI refer, becomes



$$RCOCHN_2 + HOAc = \overset{\delta-}{AcO}\text{-----}\underset{\substack{|\\ RCO\ (B)}}{CH_2}\text{-----}\overset{\delta+}{N_2} \quad (21)$$

where B is the transition-state of the reaction (20). The relatively high negative values of the entropies of activation may well be associated with the fixation (freezing) in the process of solvent molecules on this polar transition-state.[16]

The plot of Fig. 6,[1] then, represents a linear free energy relationship between process (21) and the ionization of *p*-substituted benzoic acids. The negative values of the slopes (ρ) may be interpreted as indicating that the primary effect of the substituents is on the ability of the diazoketone to accept a proton in reaction (19).

Acknowledgments.—The authors wish to express their thanks to the Rutgers University Research Council for a grant-in-aid for the academic year 1949–1950 which materially expedited the completion of this research, and also to Dr. Edward L. Simons of this Laboratory for his assistance in the development of the graphical method for analyzing kinetic data presented in this paper.

---

[16] The entropy of freezing one mole of acetic acid is −9.5 e.u.

NEW BRUNSWICK, NEW JERSEY

RECEIVED SEPTEMBER 25, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Studies on the Pinacol Rearrangement. I. The Composition of Products Obtained in Some Reactions of 1,1,2-Triphenyl-2-bromoethanol

BY JOHN F. LANE AND DAVID R. WALTERS[1]

1,1,2-Triphenyl-2-bromoethanol (I), a new compound, has been synthesized, and the products formed when it is acted upon by various basic and electrophilic reagents, as well as aqueous dioxane, have been determined quantitatively. Bases produce pure triphenylethylene oxide (II) while silver and mercuric ion lead to the exclusive formation of phenyl benzhydryl ketone (III). Solvolysis in aqueous dioxane produces a mixture of ketone (III) and triphenylethylene glycol (IV) in which the former predominates. Structures for the transition states which lead to the formation of oxide, ketone and glycol are discussed.

That halohydrins, $R_1R_2COH{-}CXR_3R_4$, easily undergo the pinacol rearrangement to give ketones ($R_1COCR_2R_3R_4$) is well known.[2] Such transformations have been especially extensively studied by Tiffeneau and his students, who have shown that agents for rearrangement include silver and mercuric oxides and dry potassium hydroxide, the latter usually giving appreciable (often predominant) amounts of epoxides $R_1R_2C\overset{O}{\diagup\!\diagdown}CR_3R_4$.[3]

It has been shown recently by Winstein and his students[4] that in simple halohydrins, $\gt COH{-}CX\lt$, the hydroxyl group on C_β contributes a substantial driving force (L_0 = 1.34 kcal.) toward facilitating release of the halogen at C_α through formation of intermediates $\gt C\overset{\overset{H\oplus}{O}}{\diagup\!\diagdown}C\lt$. Moreover, if the hydroxyl is converted by the action of a base to an alkoxide ion, an even larger driving force results (L_0 = 6 kcal.).

---

[1] du Pont Fellow in Chemistry, Rutgers University, 1946–1948.

[2] *Cf.* J. W. Baker, "Tautomerism," Routledge, London, 1934, p. 295 *et seq.*

[3] For typical examples see M. Tiffeneau, *et al.*, *Bull. soc. chim.*, **29**, 782 (1921); **33**, 725 (1923); **37**, 430, 1410 (1925); *Compt. rend.*, **134**, 1505 (1902); **145**, 811 (1907).

[4] *Cf.* S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948) and earlier papers.