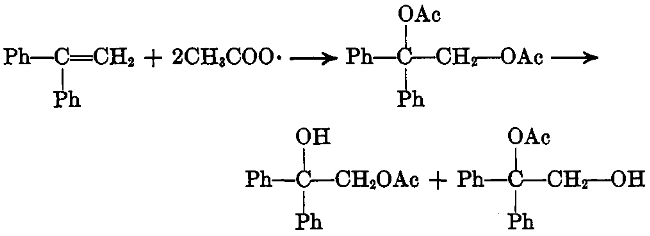
ments, it was similarly shown that the carbon monoxide was produced in the cathode section. Attempts to isolate IV were unsuccessful.

Although the electrolysis of esters[8] does not always result in an acyl–oxygen displacement, evidence for such reactions may be inferred from some of the products reported by Bonner and Mango.[2b] These were isolated after the electrolysis of sodium acetate–acetic acid in the presence of 1,1-diphenylethane.



$$Ph{-}C(Ph){=}CH_2 + 2CH_3COO\cdot \longrightarrow Ph{-}C(OAc)(Ph){-}CH_2{-}OAc \longrightarrow Ph{-}C(OH)(Ph){-}CH_2OAc + Ph{-}C(OAc)(Ph){-}CH_2{-}OH$$

Experimental

Electrolysis of Triphenylacetic Acid in Dimethylformamide.—The electrodes consisted of two pieces of smooth platinum foil (2 × 3 cm.) attached to short lengths of platinum wire. These were sealed into glass tubing which extended down from a ₸ 45/50 (male) glass head, which also held a 24/40 joint for a condenser. The glass tubes were filled with mercury to make power connections, and the electrodes were spaced 0.5 in. apart. The cell compartment (160 ml.) was fitted to receive the electrode unit and was equipped with a nitrogen gas inlet, a thermometer well, a water jacket for cooling, and a magnetic stirring bar. A refrigerated, circulating bath was used to maintain the solution temperature at 25–30°. The d.c. power supply had an output of 150 v., 15 amp.

The CO_2 was determined by using an Ascarite-filled absorption bulb connected to the condenser through a cold finger trap.

The cell was charged with a solution of 5.76 g. (0.02 mole) of triphenylacetic acid[9] and 0.6 ml. of triethylamine in 60 ml. of purified dimethylformamide. Electrolysis was continued for 2 hr. and 50 min., at a current density of 16.7 ma./cm.^{2} (100–150 v.). A total of 48.1 mg. (5.5%) of CO_2 was collected. The evolution of CO was detected by the darkening of a strip of absorbent paper soaked with a $PdCl_2$ solution.

The resulting solution was diluted with water to precipitate most of the products. Separation was accomplished by chromatography on alumina. Elution with *n*-hexane afforded 110 mg. (3%) of triphenylmethane, m.p. 93° (lit.[10] m.p. 92°). Further elution with benzene gave 3.6 g. of I, m.p. 175–177°, $\gamma_{C=O}$ 5.75, 5.90 μ.

Anal. Calcd. for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.84; N, 3.90. Found: C, 76.89; H, 5.90; N, 3.83.

In a similar manner, 5.76 g. (0.02 mole) of triphenylacetic acid and 0.6 ml. of triethylamine in 60 ml. of purified dimethylformamide was electrolyzed for 5 hr. during which time the current density dropped from 16.7 to 4.6 ma./cm.^{2} (100–150 v.). A total of 289 mg. (33%) of CO_2 was collected, and CO was qualitatively detected. Chromatography gave 3.87 g. (81%) of triphenylmethane which was the only product which could be isolated.

A modified H-tube, equipped with a medium glass frit to allow separated electrode compartments, was fitted with circular smooth platinum disk electrodes. A condenser, cold trap, and gas absorption bulb were connected to each compartment. Provisions to detect CO from each electrode were also made.

Into each compartment was placed a solution containing 2.88 g. (0.01 mole) of triphenylacetic acid, 0.8 ml. of triethylamine, 0.72 g. (0.002 mole) of ester I, and 30 ml. of dimethylformamide. The electrolysis was carried out for 13 hr. at a current density of 1.4–0.5 ma./cm.^{2}. The solution in the anode compartment became darker in color than that in the cathode compartment, and continuous gassing was observed at the cathode. The evolution of CO was evident only at the cathode. After removing the solvent under reduced pressure, the residue from each compartment was dissolved in ether and extracted with Na_2CO_3 solution. No acid was found. The residue from the anode was 4.33 g., while 2.45 g. was obtained from the cathode compartment. Thin layer chromatography of the residues showed that triphenylmethane was present in both compartments, although some migration between them appears to have occurred. An electroosmotic effect resulted in an increase of solution volume in the cathode compartment during the electrolysis.

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[8] (a) T. Okubo and S. Tsutsumi, *Tech. Rept. Osaka Univ.*, **13**, 495 (1963); (b) T. Okubo and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **37**, 1794 (1964).

[9] J. Schmidlin, *Ber.*, **39**, 634 (1906).

[10] J. F. Norris, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 548.

Reactions of Nitro Alcohols. II.[1] The Kinetics of Dissociation of 2,2-Dinitropropanol in Aqueous Buffers

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The rates of dissociation of 2,2-dinitropropanol to formaldehyde and the carbanion of 1,1-dinitroethane were measured in aqueous buffers at precisely controlled temperatures near 10, 25, and 40°. The kinetic data are consistent with the following dissociation mechanism: rapid ionization of the carbinol to $CH_3C(NO_2)_2CH_2O^-$, followed by slow dissociation, by a reversible reaction, to the products. The bimolecular rate constant for the reaction of formaldehyde and the carbanion of 1,1-dinitroethane was evaluated at each temperature; E_a, ΔH^*, and ΔS^* for the reaction of these species were found to be 18.8 kcal. mole^{-1}, 18.2 kcal. mole^{-1}, and +1.5 e.u., respectively.

The dissociation of 2,2-dinitropropanol (A) and of four other polynitromethylcarbinols has been shown to be a pH-dependent equilibrium of the form represented by eq. 1.[1] The equilibrium constant, *K*, for

$$\underset{A}{CH_3C(NO_2)_2CH_2OH} + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{B}{CH_3C(NO_2)_2^-} + \underset{C}{CH_2(OH)_2} \quad (1)$$

(1) was determined for aqueous phosphate buffers of ionic strength 0.1. It was noticed that the steady-state concentrations were attained rather slowly. The purpose of this study is to measure and interpret these equilibration rates.

Experimental

Apparatus and Chemicals.—2,2-Dinitropropanol was made by the reaction of formaldehyde with 1,1-dinitroethane, which, in turn, was made from 1-chloro-1-nitroethane by the ter Meer

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[1] Paper I: T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

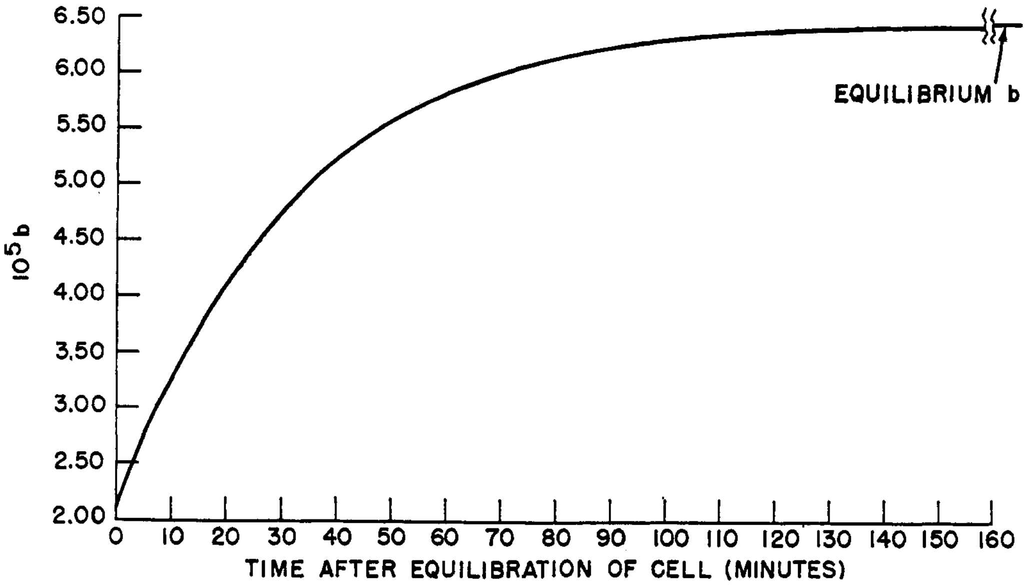

Figure 1.—Typical plot showing the smooth dissociation of 2,2-dinitropropanol to the carbanion of 1,1-dinitroethane; b = $[CH_2C(NO_2)_2^-]$, t = 25.14°, pH 6.26 (phthalate buffer).

reaction[2]; the carbinol was recrystallized from an azeotropically dried chloroform solution.

Phosphate buffers were made from 0.1 M KH_2PO_4 and 0.1 N NaOH according to the specifications of Clark and Lubs[3]; sufficient NaCl was added to make the ionic strength 0.1 after the final dilution. For the phosphate buffer of pH 6.26 (25°), 50.0 ml. of 0.1 M KH_2PO_4 and 10.0 ml. of 0.1 N NaOH/100 ml. were used; for the phosphate buffer of pH 6.21 (25°), these volumes were 25.0 and 5.0 ml., respectively. The phthalate buffers (25 and 40°) were made by diluting 36.0 ml. of 0.1 M potassium hydrogen phthalate and 33.0 ml. of 0.1 N NaOH to 100.0 ml.; after mixing, such solutions have an ionic strength of 0.1. The pH of the buffer solutions was measured by the procedure given in ref. 1, using 0.025 M KH_2PO_4–0.025 M Na_2HPO_4 as reference and the pH values for this solution given by Bates.[4]

For the 10° rate measurements, a Beckman DU spectrophotometer fitted with a special thermostated cell compartment[1] was used; temperature variation was ±0.02° in the compartment; the sample cell was assumed to have the path length, 0.0299 cm., stated by the manufacturer (The American Instrument Co., Silver Spring, Md.). All other rate measurements were made with a Cary Model 14 recording spectrophotometer, fitted with the temperature-controlled cell compartment provided by the manufacturer; estimated temperature variation was ±0.05°; 1.00-cm. cells, provided by The Optical Cell Co., Brentwood, Md., were used.

Spectrophotometric Determination of Concentrations of B.—Solutions of A, partially or fully dissociated to B, were analyzed for B by measuring the optical density at $t°$ and 382 mμ (λ_{max} for B). The molar concentration of B, b, was then calculated from the molar extinction coefficient for B at 382 mμ (ϵ); for 10 and 25°, ϵ was taken from ref. 1; for 40°, ϵ was determined by the method of ref. 1 to be 16,720. Absorption due to A, C, and $CH_3C(NO_2)_2H$ is negligible at 382 mμ.[1] The formal concentration of A in a stock solution was determined by diluting quantitatively a measured volume of the stock solution with 0.1 N NaOH, thereby converting all of A to B + C[1]; b was then determined spectrophotometrically, and the composition of the stock solution was calculated.

Dissociation Rates.—A 100-ml. volumetric flask containing the proper[5] buffer components and sufficient water to bring the volume to about 97 ml. was brought to $t°$. An appropriate volume of the stock solution of A was delivered from a microburet into the flask, and a rapid quantitative dilution was made. A portion of the solution was poured into the optical cell, and the optical density at 382 mμ and $t°$ was recorded *vs.* time as soon as temperature equilibration was attained. For the 25 and 40° rate measurements, the cell was immersed in the temperature bath for about 2 min. to hasten temperature equilibration. The results of a typical run are shown in Figure 1. It should be noted that zero time is arbitrary. The initial value of b was always found to be greater than 0; the reason is that A is partially dissociated to B in the stock solutions of A. For each pH studied the equilibrium values of b are drift free, thus showing the absence of slow side reactions.

Initial Association Rates.—Into a 100-ml. volumetric flask containing 5.70 ml. of 0.1 N NaOH was delivered the appropriate volume of a stock solution of A having a formal molarity of 0.0287. After mixing, all A in such a solution is converted to B + C.[1] Fifty milliliters of 0.1 M KH_2PO_4 was then added and a rapid quantitative dilution was made. A dry 1.00-cm. cell was filled with a portion of this solution, and then brought to 25.15° by immersion in the constant-temperature bath. The cell was then dried and the optical density at 382 mμ was recorded *vs.* time on the Cary spectrophotometer. The initial value of db/dt was then determined from the time required for the optical density to decrease by 0.02 units. For the same b, duplicate determinations of the initial value of db/dt were within 10% of each other, and so were averaged. Figure 2 shows the change of such initial db/dt values with the value of b corresponding to a decrease in the optical density of 0.01 units. In this plot, the range of b could not be increased because of the following experimental problems: (i) increasing b made the rate so fast that it could hardly be called initial, and (ii) decreasing b made the rate so slow that instrument drift became an important error. Furthermore, changing the pH did not obviate these difficulties because the initial rate appeared to be pH independent.

Rate Equation for the Equilibration of A with B and C

The simple mechanisms for the equilibration of A with its dissociation products fall into two classes. One class, which includes reaction 1, requires that the rate of formation of A from its dissociation products, $(da/dt)_f$, be proportional to b^2. The other class, which includes mechanism 2, requires that $(da/dt)_f$ be proportional to b. We can obtain a good estimate of $-(da/dt)_f$ by measuring the initial change of b with time, $(db/dt)_0$, for a solution of A whose pH has been rapidly changed from that required for complete

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[2] O. H. Johnson, NAVORD Report (NOL) 2448, June 6, 1952, p. 5. Available to the general public through The Office of Technical Services, Department of Commerce, Washington 25, D. C.

[3] See H. T. S. Britton, "Hydrogen Ions," 4th Ed., D. Van Nostrand Co., Inc., Princeton, N. J., 1956, p. 358.

[4] R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 76.

[5] The buffer components were chosen to give conveniently measured rates and a steady-state optical density indicating partial dissociation of A.

$$\mathrm{CH_3C(NO_2)_2CH_2OH + H_2O \underset{slow}{\overset{fast}{\rightleftharpoons}} CH_3C(NO_2)_2H + CH_2(OH_2)} \quad (2)$$

$$\mathrm{CH_3C(NO_2)_2H \rightleftharpoons CH_3C(NO_2)_2^- + H^+}$$

dissociation (0.1 N NaOH) to that required for partial dissociation. The approximation involved is that the contribution of the dissociation reaction to $(\mathrm{d}b/\mathrm{d}t)_0$ is negligible. A plot of log $(-\mathrm{d}b/\mathrm{d}t)_0$ *vs.* log b_0 was found to have a slope of 2 (see Figure 2). Thus, the second class of mechanisms is eliminated, and we will consider only the first class.

For a solution of A in the process of equilibration at constant pH, equilibration mechanism 1 requires that b change with time according to eq. 3. In this equation, b_e is the equilibrium value of b, K the equilibrium

$$\ln\left[\frac{(b_e - b)(b_e + KK_w/d)}{b_e(b_e + b + KK_w/d)}\right] = -k_2(1 + d/K_i)(2b_e + KK_w/d)t \quad (3)$$

constant for (1), K_w the ionization constant of water,[6] K_i the ionization constant for $\mathrm{CH_3C(NO_2)_2H}$, and d the activity of hydrogen ion. The factor $(1 + d/K_i)$ arises because one must allow for partial association of B to $\mathrm{CH_3C(NO_2)_2H}$. For the 10 and 25° runs, values of K and K_i for phosphate buffers of ionic strength 0.1 were taken from ref. 1. For the 40° runs, values of K and $(1 + d/K_i)$ were determined to be 1.81×10^4 and 1.00, respectively, by using the procedures described in ref. 1.

Plots of log $(b_e - b)/(b_e + b + KK_w/d)$ *vs.* time were found to be linear for all kinetic runs (see Figure 3), thus giving strong evidence that (1) or its kinetic equivalent is the equilibration mechanism. However, k_2 cannot be evaluated from (3) by least-square methods because all times were measured relative to an arbitrary rather to the actual (unknown) zero time. Fortunately, application of the Guggenheim method for first-order reactions[7] to eq. 3 gives (4) from which k_2 can be evaluated by least-square methods. In (4), b' is the value of b at time $(t + \Delta)$, and e is a constant

$$\ln\left(\frac{b' - b_e}{b_e + b' + KK_w/d} - \frac{b - b_e}{b_e + b + KK_w/d}\right) = -k_2(1 + d/K_i)(2b_e + KK_w/d)t + e \quad (4)$$

dependent on Δ and k_2 but independent of b and b'. For each kinetic run, values of k_2 were calculated by the least-square method from eq. 4 for three values of Δ, using the value of e which gave the best linear fit[8] and values of t covering 1.5–3Δ. For each run, the values of k_2 were nearly independent of Δ. For example, for the typical run shown in Figure 1, values of k_2 (in M^{-1} sec.$^{-1}$) for $\Delta = 40$, 50, and 60 min. were found to be 0.613_8, 0.615_2, and 0.614_1, respectively. The value of k_2 for each run was taken to be the average of the three k_2 values so computed, and the value of k_2 for buffer composition was taken as the average of all of the runs made for that composition. Table I summarizes the values of k_2 for independent variation of temperature and buffer composition. The calculation of k_1 for (1) as k_2K was not considered justified at this point (*vide infra*).

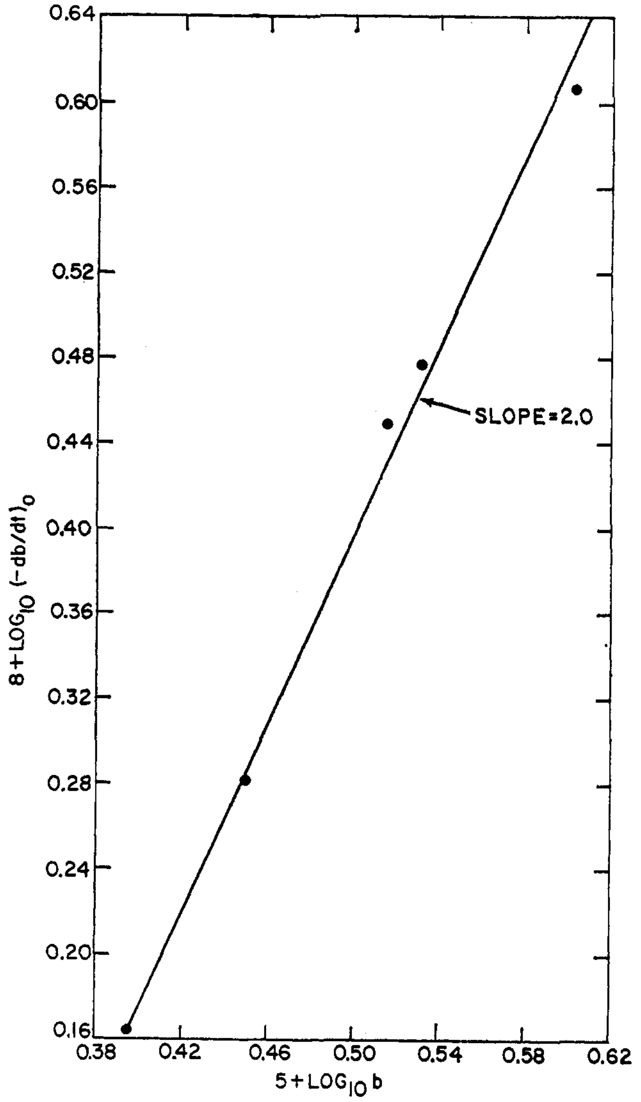

Figure 2.—Plot showing the effect of changing $[\mathrm{CH_3C(NO_2)_2^-}]$, b, on the initial rate of reaction of the carbanion of 1,1-dinitroethane and formaldehyde.

Table I

Effect of Temperature and Buffer Composition on k_2, the Bimolecular Rate Constant for the Reaction of $\mathrm{CH_3C(NO_2)_2^-}$ and $\mathrm{CH_2(OH)_2}$ in Water

Temp., °C.	pH	$[\mathrm{HPO_4^{-2}}]$	No. of runs	Av. k_2[a] ± av. dev.
9.64	6.73	0.019	8	$0.130_3 \pm 0.0042$
25.14	6.26	*b*	4	$0.58_6 \pm 0.015$
	6.26	0.010	3	$0.59_9 \pm 0.005$
	6.21	0.005	3	$0.62_7 \pm 0.010$
	6.48	0.015	4	$0.61_9 \pm 0.012$
40.16	6.32	*b*	8	$3.2_6 \pm 0.08$

[a] In M^{-1} sec.$^{-1}$; ionic strength 0.1. [b] Potassium hydrogen phthalate + sodium hydroxide buffer.

Conclusions and Discussion

Two important conclusions are clear. (i) Within the error of pH measurement, k_2 is independent of pH, buffer concentration, and buffer composition. (ii) The rate of dissociation of A, measured by k_1 or k_2K, is

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[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 645.

[7] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[8] Values of k_2 calculated from e, although not precise, did agree well with those calculated from the slopes.

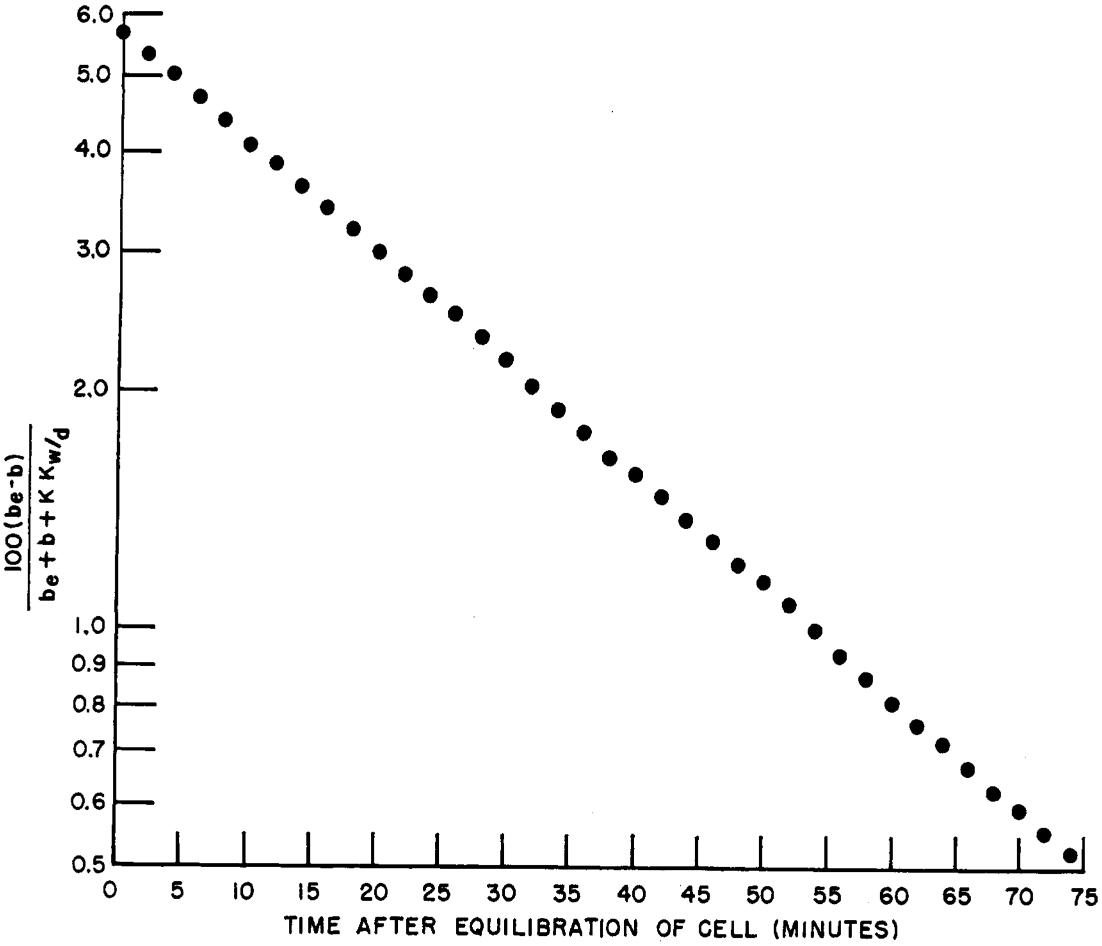

Figure 3.—Plot showing the fit of eq. 3 to the data plotted in Figure 1.

subject to specific catalysis by OH^-. The kinetic equivalents of mechanism 1 will now be discussed in light of these conclusions.

Equilibration mechanism 5 is consistent with the observed proportionality of log $(b_e - b)/(b_e + b + KK_w/d)$ with time and the dependence of $(da/dt)_f$ on b^2. However, mechanism 5 can be definitely ruled out because it requires the rate of reaction of B and C to be proportional to rather than independent of d.

$$CH_3C(NO_2)_2CH_2OH + H_2O \xrightleftharpoons{\text{slow}} CH_3C(NO_2)_2^- + CH_2(OH)(OH_2)^+ \quad (5)$$

$$CH_2(OH)(OH_2)^+ \xrightleftharpoons{\text{fast}} CH_2(OH)_2 + H^+$$

Mechanism 1 does not give a satisfactory explanation for the lack of detectable catalysis by HPO_4^{-2}.[9] This apparent anomaly can be resolved if mechanism 1 is replaced by its kinetic equivalent, mechanism 6.

$$CH_3C(NO_2)_2CH_2OH + X \xrightleftharpoons{\text{fast}} CH_3C(NO_2)_2CH_2O^- + XH^+ \ (X = \text{general base}) \quad (6)$$

$$CH_3C(NO_2)_2CH_2O^- + H_2O \xrightleftharpoons[k_2]{k_1'} CH_3C(NO_2)_2^- + CH_2(OH)_2$$

Mechanism 6 gives specific catalysis by OH^- for any base (OH^-, HPO_4^{-2}, phthalate anion, etc.). Clearly, for mechanism 6, k_2 is still the bimolecular rate constant for the reaction of B and C, while k_1' is k_1/K', where K' is the unreported equilibrium constant for (7). The dissociation of $CH_3C(NO_2)_2CH_2OH$ or $CH_3C(NO_2)_2CH_2O^-$ requires that negative charge be transferred to the 2-carbon and its nitro groups in the transition state; it may be that negative charge can be more readily transferred from $CH_3C(NO_2)_2CH_2O^-$ than from OH^-, thus accounting for the preference of mechanism 6 over 1.

$$CH_3C(NO_2)_2CH_2OH + OH^- \rightleftharpoons CH_3C(NO_2)_2CH_2O^- + H_2O \quad (7)$$

Using the values of k_2 for 9.64 and 40.16° in Table I and the over-all average of all k_2 values for 25.14°, the values of E_a, ΔH^*, and ΔS^* for the reaction of B and C are found to be 18.8 kcal. mole^{-1}, 18.2 kcal. mole^{-1}, and +1.5 e.u., respectively. The activation energy for the reaction of B and C is essentially the same as that for reaction 8 in dioxane, 19 kcal. mole^{-1}.[10]

$$CH_3CH_2CH_2CH(OC_2H_5)_2 + (NO_2)_3CH \longrightarrow CH_3CH_2CH_2CH(OC_2H_5)C(NO_2)_3 + C_2H_5OH \quad (8)$$

The close agreement of E_a values is probably coincidental because reaction 8 occurs *via* the alkoxycarbonium ion $CH_3CH_2C^+H(OC_2H_5)$.[10]

Acknowledgment.—The author would like to thank Dr. D. V. Sickman for advice and encouragement and Dr. J. R. Holden for writing the program for the IBM 7090 used for the least-squares calculations.

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[9] Toward saturated carbon, HPO_4^{-2} and OH^- have nearly the same nucleophilicity: C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953). Further, $[HPO_4^{-2}]$ is about 10^6 times the activity of OH^- in the buffers used for the rate measurements.

[10] C. S. Rondestvedt, Jr., M. Stiles, and A. L. Krieger, *Tetrahedron Suppl.*, **1**, 197 (1963).