Reactions of Nitro Alcohols. I. The Dissociation Constants of Some 2-Substituted Derivatives of 2,2-Dinitroethanol in Water

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Received July 27, 1964

For aqueous solutions at precisely controlled temperatures near 10 and 25°, the ionization constant, K_i, for $Z(NO_2)_2CH$, and the equilibrium constant, K, for the reaction, $Z(NO_2)_2CCH_2OH + OH^- \leftrightharpoons Z(NO_2)_2C^- + CH_2(OH)_2$, have been determined for Z = CH_3, Cl, Br, NO_2, and CN. The ionic strength was kept at 0.1. It was found that $\log (K/K_i) = 9.7$ is a good approximation for all Z at 25°. The effect of changing Z or K can be rationalized in terms of changes of the electrostatic energy and resonance stabilization of the carbanion $Z(NO_2)_2C^-$ with Z.

In 1895 Henry discovered that a mononitroparaffin, RH, and an aliphatic aldehyde, R′CHO, condense to the nitro alcohol, RCH(R′)OH.[1] Using formaldehyde and nitroform, the Henry reaction gives good yields of 2,2,2-trinitroethanol.[2,3] Evidence has been presented that the latter preparation involves an equilibrium of the form represented by the equation, $(NO_2)_3CCH_2OH + OH^- \rightleftarrows (NO_2)_3C^- + CH_2(OH)_2$.[4,5] In this equation the formaldehyde is shown as $CH_2(OH)_2$ because it is 99.9% hydrated in dilute aqueous solution at room temperature,[6] and the nitroform is shown in the ionized form because conditions which cause partial dissociation of the carbinol also cause nearly complete ionization of the nitroform.[5]

Carbinols derived from nitroform and other carbonyl compounds, $(NO_2)_3CC(R_1)(R_2)OH$, are generally much less stable than trinitroethanol in water. The extent of cleavage at room temperature has been found to increase in the following order: R_1,R_2 = H,H < H,CH_3 < $(CH_2)_3$ < CH_3,CH_3.[5] This report deals with the effect of structural changes on the aqueous cleavage of carbinols derived from formaldehyde and derivatives of dinitromethane, $Z(NO_2)_2CH$.

Experimental

Apparatus.—A Beckman DU spectrophotometer whose wavelength scale was calibrated against a mercury lamp was fitted with a special stainless steel cell compartment having quartz windows. Distilled water from a reservoir placed in a constant-temperature bath was pumped through the cell compartment, taking particular care to avoid the introduction of air bubbles. The temperature of the cell compartment was measured with a 0–50° thermometer, graduated in tenths of a degree, and calibrated against a similar thermometer bearing a National Bureau of Standards calibration certificate. The temperature of the cell compartment was found to vary no more than ±0.02°. The absorption cells had fused quartz windows, were supplied by the American Instrument Co., Silver Spring, Md., and were assumed to have the path length specified (0.0299 cm. except where noted otherwise). A Beckman Model G pH meter, a set of class S metric weights, a 50-ml. buret, and a 5-ml. microburet (both calibrated) were also used.

Chemicals.—*Caution.* All nitroparaffin derivatives used in this study are explosives, and due care (safety glasses, shields, etc.) must be used in handling the pure compounds. Scraping or grinding of the pure solids, particularly the potassium dinitromethides, *must* be avoided.

The following compounds were made and purified according to the methods given in the literature, with the modifications noted: potassium 1,1-dinitroethide[7]; potassium dinitrocyanomethide[8]; nitroform,[9] crystallized from hexane; 2,2-dinitropropanol,[10] crystallized from an azeotropically dried chloroform solution; 2,2,2-trinitroethanol[11]; 2-bromo-2,2-dinitroethanol,[12] crystallized from an azeotropically dried methylene chloride solution; and 2-chloro-2,2-dinitroethanol, made by chlorinating the potassium salt of 2,2-dinitroethanol.[13]

The potassium bromo- and chlorodinitromethides were made by the following procedure. A 1.0-g. sample of the 2-halo-2,2-dinitroethanol was dissolved in 10 ml. of methanol contained in a 20-ml. beaker; a solution of 1.0 g. of potassium hydroxide in 5 ml. of 50% (by volume) aqueous methanol was added dropwise to the magnetically stirred, cooled carbinol solution until the precipitated potassium halodinitromethide made the solution too thick to be stirred. The yellow precipitate was collected and washed with cold 2% potassium hydroxide in 50% aqueous methanol and then cold 50% aqueous methanol. After air drying, the yield was found to be about 50%.[14] The potassium chlorodinitromethide was found to be unstable in the free state at room temperature and was used to make an aqueous stock solution after air drying for 2 hr. The potassium bromodinitromethide was recrystallized from 2% aqueous potassium hydroxide and air dried for 16 hr.

Anal. Calcd. for $CBrKN_2O_4$: C, 5.38; Br, 35.83; K, 17.53; N, 12.56. Found: C, 6.29 and 6.22; Br, 35.53 and 35.78; K, 17.56; N, 10.72.

Mild explosions during the combustion prevented accurate analyses for carbon and nitrogen.

Aqueous formaldehyde solutions were made as follows. A suspension of paraformaldehyde in distilled water containing a drop of concentrated sulfuric acid per 500 ml. of water was heated on the steam bath and stirred magnetically for 24 hr. The solution was cooled, filtered to remove turbidity, and analyzed by Walker's sulfite method,[15] neutralizing before transfer to the excess sodium sulfite.

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(1) L. Henry, *Compt. rend.*, **120**, 1265 (1895); **121**, 210 (1895).

(2) N. S. Marans and R. P. Zelinski, *J. Am. Chem. Soc.*, **72**, 5329 (1950).

(3) References to work done in this country and in Germany prior to the work of Marans and Zelinski are given in the following report: K. Klager and M. B. Frankel, "A Review of Nitroform and 2,2,2-Trinitroethanol," Aerojet Engineering Corp., Azusa, Calif., Feb., 1951, p. 44. This report is available to the general public through Defense Documentation Center, Cameron Station, Alexandria, Va.

(4) (a) D. Luckey, NAVORD Report (NOL) 1717, U. S. Naval Ordnance Laboratory, Sept., 1950. Available to the general public through Office of Technical Services, Dept. of Commerce, Washington 25, D. C. (b) J. Reinhart, J. G. Meitner, and R. W. Van Dolah, *J. Am. Chem. Soc.*, **77**, 496 (1955).

(5) T. N. Hall, *Tetrahedron. Suppl.*, [1] **19**, 115 (1963). The dissociation constant for 2,2,2-trinitroethanol has been redetermined in the present study, using more precise measurements.

(6) L. C. Gruen and P. T. McTigue, *J. Chem. Soc.*, 5217 (1963).

(7) E. ter Meer, *Ann.*, **181**, 4 (1877).

(8) C. O. Parker, W. D. Emmons, H. A. Rolewiez, and K. S. McCallum, *Tetrahedron*, **17**, 79 (1962).

(9) See ref. 3, p. 1, Appendix B.

(10) O. H. Johnson, NAVORD Report (NOL) 2448, "The Preparation and Properties of Bis(2,2-Dinitropropyl) Nitramine," June, 1952, p. 5. See ref. 4a for availability.

(11) K. G. Shipp and M. E. Hill, NAVORD Report (NOL) 6752, "An Improved Process for the Preparation of 2,2,2-Trinitroethanol," Feb., 1960, p. 14. See ref. 4a for availability.

(12) M. B. Frankel, *J. Org. Chem.*, **23**, 813 (1958).

(13) K. G. Shipp, U. S. Naval Ordnance Laboratory, Silver Spring, Md., first synthesized this compound by the method cited, and kindly furnished a pure sample. The synthetic procedure will be published shortly.

(14) The yields were estimated from the weights of slightly damp salts. The salts were considered too sensitive to initiation by scraping to be conveniently weighed.

(15) J. F. Walker, "Formaldehyde," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1953, p. 383.

National Bureau of Standards standard sample 84e of potassium hydrogen phthalate, after drying at 125°, was used to standardize aqueous sodium hydroxide solutions. The latter solutions were then used to analyze sulfuric and hydrochloric acid solutions. U.S.P. paraformaldehyde and all other chemicals, which were Fisher Certified reagent grade, were used without further purification.

Preparation of Aqueous Buffer Solutions and Measurement of pH.—Aqueous buffer solutions of approximately the desired pH were made up according to the specifications of Clark and Lubs[16] except that sufficient sodium chloride or potassium chloride was added to make the ionic strength 0.1 after dilution. The actual pH of such a buffer solution (unknown buffer) was measured at constant temperature with a pH meter using one of the following solutions for standardization: 0.1 M HCl, 0.05 M potassium hydrogen phthalate, and 0.025 M KH_2PO_4 + 0.025 M Na_2HPO_4. The unknown buffer and the standard which most closely matched its pH were placed in beakers surrounded by a bath whose temperature varied no more than ±0.05°. After allowing 30 min. for temperature equilibration of the solutions and electrodes, the pH meter was standardized using the pH cited in the literature[17a,18] as the pH of the standard. The electrodes were rinsed with water at the bath temperature and placed in the unknown buffer; the pH was read after 1 min. Five such determinations (including restandardization) usually ranged over no more than 0.03 pH unit and were averaged to give the pH reported.

Dissociation Constant for $Z(NO_2)_2CCH_2OH$, Z = CH_3, Cl, Br, NO_2.—The dissociation reaction was assumed to be represented by eq. 1. The method briefly outlined in ref. 5 was used to

$$Z(NO_2)_2CCH_2OH + OH^- \rightleftarrows Z(NO_2)_2C^- + CH_2(OH)_2 \quad (1)$$

determine the concentrations of the species in reaction 1. One measures the amount of the carbanion $Z(NO_2)_2C^-$ produced by the dissociation of a known amount of carbinol dissolved in a suitable aqueous buffer having an ionic strength μ of 0.1.[19] The optical density of this buffer solution at λ_{max} for $Z(NO_2)_2C^-$, and the molar extinction coefficient for $Z(NO_2)_2C^-$ at λ_{max} (ϵ) are then used to calculate $[Z(NO_2)_2C^-]$ for the buffer solution.[20a] The value of the hydroxide ion activity was calculated from the measured pH of the buffer solution and the ionization constant for water. The concentration of formaldehyde was not measured but calculated from the assumed stoichiometry as $[Z(NO_2)_2C^-] + [Z(NO_2)_2CH]$. For the buffer solution the value of $[Z(NO_2)_2CH]$ was calculated from the measured pH and $[Z(NO_2)_2C^-]$, and from an independently determined value for the pK_i of $Z(NO_2)_2CH$ at $\mu = 0.1$. Finally, the value of $[Z(NO_2)_2CCH_2OH]$ for the buffer solution was calculated as the total amount of carbinol added to the buffer, in concentration units based on the final dilution, less $[CH_2(OH)_2]$.

It is clear that the following determinations provide sufficient data to calculate the equilibrium constant for reaction 1.

(i) The Molar Extinction Coefficient for $Z(NO_2)_2C^-$ at λ_{max} (ϵ).—The following substances are quite stable at room temperature, are easily purified and completely dissociated to $Z(NO_2)_2C^-$ in dilute aqueous 0.1 N NaOH, and were selected as standards for ϵ: $CH_3(NO_2)_2CK$, $Cl(NO_2)_2CCH_2OH$, $Br(NO_2)_2CK$ (sample used for microanalysis), and $(NO_2)_3CH$. Appropriate amounts of the first three substances were weighed out, dissolved in water, and diluted quantitatively at t° with water and sufficient aqueous NaOH to make the final solution 0.1 N in NaOH. Nitroform is too hygroscopic to be weighed conveniently. Instead, aliquots of an aqueous stock solution of nitroform were assayed by titration with standard 0.1 aqueous NaOH[21b]; an aliquot of this stock solution was diluted quantitatively at 25° with water and sufficient aqueous NaOH to make the final solution 0.1 N in NaOH. The optical densities of these 0.1 N NaOH solutions were measured at λ_{max} for $Z(NO_2)_2C^-$ and t° after a steady state was attained, and the values of ϵ were calculated.[21] After the optical density of the nitroform solution had been measured at 25° and 350 mμ, the temperature of the cell compartment was lowered to 9.6° and the optical density was measured after temperature equilibration; a value of ϵ for 9.6° was then calculated, making a correction for the volume change of the solution based on the density of pure water at 10 and 25°.

(ii) Analysis of Stock Solutions of $Z(NO_2)_2CCH_2OH$, $Z(NO_2)_2CH$, and $Z(NO_2)_2CK$.—Analysis of these solutions is illustrated by the method used for the carbinols. A volume, v_1 ml., of the carbinol stock solution was diluted to V_1 ml. at t° with 0.1 N aqueous NaOH. The optical density of this solution at λ_{max} for $Z(NO_2)_2C^-$ and t°, D_1, was then measured after a steady state was attained. The carbinol concentration of the stock solution was then calculated from these data and ϵ was calculated at t°, making sure that the Beer–Lambert law was obeyed for the concentration ranges involved. Stock solutions of $Z(NO_2)_2CH$ and $Z(NO_2)_2CK$ were analyzed in a similar manner.

(iii) Analysis of Buffered Solutions of $Z(NO_2)_2CCH_2OH$, $Z(NO_2)_2CH$, and $Z(NO_2)_2CK$.—The buffer components for such solutions were chosen to make the conversion to $Z(NO_2)_2C^-$ incomplete. The determination of $[Z(NO_2)_2C^-]$ for such solutions is illustrated for carbinol solutions. A volume, v_2 ml., of the carbinol stock solution was diluted to V_2 ml. at t° after addition of the proper buffer components and sufficient 1 N aqueous NaCl (or 1 N aqueous KCl for Z = NO_2) to make the ionic strength after dilution 0.1. The optical density at λ_{max} and t°, D_2, was then measured after a steady state was attained. Buffered solutions of $Z(NO_2)_2CH$ or $Z(NO_2)_2CK$ were analyzed in a similar manner.

The optical densities of the buffered solutions of $Cl(NO_2)_2CCH_2OH$, $CH_3(NO_2)_2CCH_2OH$, and $Br(NO_2)_2CCH_2OH$ slowly increased with time, and took as long as 3 hr. to reach the steady state. Optical densities of all solutions made according to i and ii and of $(NO_2)_3CCH_2OH$ solutions made according to iii reached the steady state within a few minutes after the final dilution, *i.e.*, in about the time required for temperature equilibration of the cell. For each Z, one of the solutions made according to iii was kept at t° for 16 hr.; the optical densities and spectral envelopes of such solutions were unchanged from the "initial steady-state measurements."

(iv) Determination of Hydroxide Ion Activity.—The pH of the buffered solutions used in iii was measured at t° (*vide supra*), and the hydroxide ion activity was calculated from the hydrogen ion activity, a, and the ionization constant for water, K_w, as K_w/a.

For values of t near 10 and 25°, the equilibrium constant for reaction 1, K, was calculated from eq. 2, using for t°, the data from determinations i → iv, the ionization constant for water,

$$K = \frac{(D_2)^2Ra}{[(D_1V_1v_2)/(V_2v_1) - D_2R](0.0299)\epsilon K_w},\ R = 1 + a/K_i \quad (2)$$

K_w,[17b] the value of ϵ given in Table I, and the value of the ionization constant for $Z(NO_2)_2CH$ at $\mu = 0.1$, K_i (see below). The calculation of K for $CH_3(NO_2)_2CCH_2OH$ at 25.13° from the following data is typical: $v_1 = 2.500$ ml., $V_1 = 249.91$ ml., $D_1 = 0.417$, $v_2 = 2.397$ ml., $V_2 = 100.01$ ml., $D_2 = 0.597$, pH $= 6.68$, $pK_i = 5.13$, $K_w = 1.012 \times 10^{-14}$, $\epsilon = 1.777 \times 10^4$, $K = 3.74 \times 10^4$. Average values of K, based on at least two determinations for each pH, are given in Table I.

Ionization Constant for $Z(NO_2)_2CH$ at $\mu = 0.1$, K_i.—The ionization constant for $Z(NO_2)_2CH$ was calculated from data obtained from determinations ii, iii, and iv above, using stock solutions of $CH_3(NO_2)_2CK$, $Cl(NO_2)_2CK$, $Br(NO_2)_2CK$, and $(NO_2)_3CH$. The calculation of K_i for $CH_3(NO_2)_2CH$ at 25.1° from the following data is typical. A solution made according to ii from 3.789 ml. of a stock solution of $CH_3(NO_2)_2CK$, diluted to 100 ml., had an optical density of 0.438 at 382 mμ and 25.1°;

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[16] N. A. Lange, "Handbook of Chemistry," Handbook Publishers Inc., Sandusky, Ohio, 1946, p. 1102.

[17] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958: (a) p. 712; (b) p. 645.

[18] R. G. Bates, "Electrometric pH Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 74.

[19] There is good evidence that the formaldehyde and carbanion liberated by the carbinol dissociation undergo no reaction except recombination to the carbinol; $Z(NO_2)_2CCH_2OH$ and $Z(NO_2)_2CH$ or $Z(NO_2)_2CK$ are completely converted to $Z(NO_2)_2C^-$ in 0.1 N aqueous sodium hydroxide solutions; the spectral envelopes of such solutions have the same shape from 300 to 430 mμ, *i.e.*, at least 40 mμ above and below λ_{max} for $Z(NO_2)_2C^-$.

[20] (a) The other species involved in the dissociation show negligible absorption at λ_{max} for $Z(NO_2)_2C^-$. For example, from Table I, ϵ for $(NO_2)_3C^-$ in aqueous 0.1 N NaOH is 1.5×10^4 at 25° and λ_{max} 350 mμ, while ϵ at 350 mμ is less than 10 for unionized nitroform in hexane or sulfuric acid (see ref. 3, p. 9) and for $CH_2(OH)_2$ in water.[6] (b) See ref. 3, p. 8.

[21] Long has very carefully determined ϵ for $(NO_2)_3C^-$ in water at 25° from 320 to 480 mμ, at 10-mμ intervals. See A. O. Long, "A Redetermination of the Molar Extinction Coefficient of Aqueous Nitroform Ion," NAVORD Report (NOL) 2480, May, 1952, p. 2. Availability is the same as ref. 4a. His value of ϵ for 25° and 350 mμ, 1.4418×10^4, is more reliable than the value given in this report, but was not used because Long does not give the temperature coefficient of ϵ.

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

Z	t, °C.	Spectral data for $Z(NO_2)_2C^-$		Equilibrium constant for reaction 1[a]		pK_i for $Z(NO_2)_2CH$
		λ_{max}, mμ	$10^4\epsilon$	pH	K	
CH_3	25.13	382	1.77_7	6.68	3.71×10^4	5.1_3[b]
				6.37	3.77×10^4	
				6.08	3.65×10^4	
	9.64	382	1.75_3	6.73	3.90×10^4	5.2_5
Cl	25.46	386	1.56_2	5.10	8.89×10^5	3.8_0
				4.91	8.91×10^5	
	9.34	386	1.62_2	5.12	8.52×10^5	3.6_2
				4.93	8.81×10^5	
Br	25.34	385	1.46_0	5.68	9.69×10^5	3.4_7
				5.28	1.00×10^6	
	10.26	385	1.47_0	5.69	9.96×10^5	3.6_4
				5.29	9.74×10^5	
NO_2	25.45	350	1.49_5[c]	1.98	3.45×10^9	0.0_6[d]
				1.62	3.41×10^9	
	9.64	350	1.51_3	1.99	4.08×10^9	0.0_5
				1.63	3.85×10^9	
CN	24.94	345	...	*e*	1.43×10^{16}	-6.2_3
	9.74	345	...	*e*	4.06×10^{16}	...

[a] Ionic strength is 0.1 except for Z = CN. [b] A. O. Long ["The Acid Strength of Some Aliphatic Nitro Compounds," NAVORD Report (NOL) 2809, March, 1953; available as in ref. 4a] reports pK_i 5.3 at ~25°, and V. I. Slovetskii, S. A. Shevelev, A. A. Fainzil'berg, and S. S. Novikov [*Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva,* **6,** 707 (1961)] report pK_i 5.21 at 20°. [c] Long has very carefully determined ϵ for $(NO_2)_3C^-$ in water at 25° from 320 to 480 mμ, at 10-mμ intervals. His value of ϵ at 350 mμ, 1.4418×10^4, is more reliable than this value but was not used in the calculation of K because his study does not give the temperature coefficient of ϵ. See A. O. Long, "A Redetermination of the Molar Extinction Coefficient of Aqueous Nitroform Ion," NAVORD Report (NOL) 2480, May, 1952, p. 2. Available as given in ref. 4a. [d] V. I. Slovetskii, S. A. Shevelev, A. A. Fainzil'berg, and S. S. Novikov [*Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva,* **6,** 599 (1961)] report pK_i 0.18 at 20°. [e] [HCl] = 2.37.

a solution of pH 6.08 made according to iii from 4.695 ml. of the same stock solution, diluted to 100 ml., had an optical density of 0.486 at 382 mμ and 25.1°. pK_i was then calculated as 6.08 + log [(4.695)(0.438)/(3.789) − 0.486]/0.486 or 5.12. A similar determination at pH 6.68 gave pK_i = 5.13. The values of K_i listed in Table I are averages of two or three determinations made in this way.

Dissociation Constant for $NC(NO_2)_2CCH_2OH$.—This carbinol is very difficult to purify[22]; excess formaldehyde is the major impurity[22] and clearly cannot be tolerated for dissociation studies. However, solid $NC(NO_2)_2CK$ is readily purified and stable. Hence, the dissociation of $NC(NO_2)_2CCH_2OH$ was studied by determining the amount of $NC(NO_2)_2C^-$ used by an aqueous acid solution of formaldehyde. Clearly, the following analyses provide sufficient data to calculate the dissociation constant.

(i) **Analysis of a Stock Solution of $NC(NO_2)_2CK$.**—A volume, v_1 ml., of the aqueous stock solution was quantitatively diluted to 100 ml. at t° with distilled water. The optical density of this solution at λ_{max} for $NC(NO_2)_2C^-$ (345 mμ) and t°, D_1, was measured in a 0.30-cm. cell after the steady state was attained.

(ii) **Analysis of Aqueous Hydrochloric Acid–Formaldehyde Solutions of $NC(NO_2)_2CK$.**—To the same volumetric flask used for i above were added v_2 ml. of the stock solution of $NC(NO_2)_2CK$, 40.0 ml. of an aqueous hydrochloric acid solution having a normality of 5.93 at 25°, and a volume, m ml., of an aqueous formaldehyde solution having a normality of M at 25°. After quantitative dilution at t° with water, the optical density of this solution at 345 mμ and t°, D_2, was measured in the same 0.30-cm. cell used for i after the steady state was attained.

The steady-state optical densities of solutions made according to i and ii were attained within a few minutes after the cell was placed in the cell compartment. One solution made according to i and one made according to ii were kept at t° for 16 hr. The optical densities at 345 mμ and the spectral envelopes were unchanged from the "initial steady state measurements." No correction was needed for the amount of $NC(NO_2)_2C^-$ converted to $NC(NO_2)_2CH$ because the latter is a very strong acid (see below).

For t = 24.94 and 9.74°, the equilibrium constant for reaction 1 for Z = CN, K, was calculated from eq. 3 and the data were obtained by procedures i and ii. In eq. 3, K_w is the ionization constant for water at t°,[17b] 2.37 = [HCl], and 2.89 is an estimate of the activity coefficient function $\frac{(f_{H^+})f_{NC(NCO_2)_2^-}}{f_{NC(NO_2)_2CCH_2OH}}$ made from Boyd's H^- function for 2.37 N HCl at 25°.[23] The value of the H^- function has not been reported for 10° and was taken equal to the value at 25°. The error introduced by this approximation is small because the H^- function for aqueous HCl molalities up to 1.2 shows very little change with temperature.[24] Other assumptions made in deriving eq. 3 are that ϵ for $NC(NO_2)_2C^-$ at λ_{max} 345 mμ is the same for water and for solutions made according to ii, so that $[NC(NO_2)_2C^-]$ for solutions made according to i and ii are $D_1/0.30\epsilon$ and $D_2/0.30\epsilon$, respectively; that $[NC(NO_2)_2CCH_2OH]$ for solutions made according to ii is the total amount of $NC(NO_2)_2C^-$ added, in concentration units based on the final dilution, less $D_2/0.30\epsilon$; and that the activity coefficient of formaldehyde is 1.

$$K = \frac{(2.37)(2.89)D_2mM}{[(D_1v_2/v_1) - D_2]100K_w} \qquad (3)$$

The calculation K for 24.94° from the following data is typical: $v_1 = v_2 = 1.600$ ml., $D_1 = 0.50_2$, $m = 50.0$ ml., $M = 7.03$, $D_2 = 0.431$, $K_w = 1.008 \times 10^{-14}$, $K = 1.45_2 \times 10^{16}$. Reproducibility is illustrated by the four values of $10^{-16}K$ for 24.94° and M = 7.03: 1.45_2, 1.40_5 for m = 50.0 and 1.41_9, 1.45_9 for m = 25.0. For 24.94 and 9.74°, the average values of K are given in Table I.

pK_i for $NC(NO_2)_2CH$.—A volume, v_1 ml. of a stock solution of $NC(NO_2)_2CK$ was diluted to 100 ml. at 25° with distilled water, and the optical density at 345 mμ, D_1, was measured in a 0.10-cm. cell. A volume, v_2 ml., of the stock solution of $NC(NO_2)_2CK$ was diluted to 100 ml. at 25° after the appropriate amount of sulfuric acid had been added; the optical density of this solution at 25° and 345 mμ, D_2, was then measured in the same 0.10-cm. cell used to obtain D_1; the weight per cent of sulfuric acid in this solution was determined by titration against standard 0.5 N NaOH. The pK was then calculated from eq. 4, using Boyd's H^- function[23](25°) for the relevant acid composition. For

$$\mathrm{p}K_i = H^- - \log D_2 + \log [(D_1v_2/v_1) - D_2] \qquad (4)$$

69.09% H_2SO_4, $v_1 = 2.000$ ml., $D_1 = 0.452$, $v_2 = 3.005$ ml., $D_2 = 0.412$, pK_i = −6.26. Similarly, for 72.22% H_2SO_4, pK_i = −6.19. Values of pK_i for 10° were not determined because the H^- function has not been reported for this temperature.

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[22] C. O. Parker, W. D. Emmons, and A. S. Pagano, *Tetrahedron,* **17,** 92 (1962).

[23] R. H. Boyd, *J. Phys. Chem.,* **67,** 737 (1963).

[24] S. S. Novikov, V. I. Slovetskii, S. A. Shevelev, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* 598 (1962).

TABLE II

QUANTITIES CALCULATED FROM EXPERIMENTAL VALUES OF K AND K_i

Z	$K_{298.15}$[a]	log (K/K_i) for 298.15°	For reaction 1: ΔH, kcal. mole^{-1}[b]	For reaction 1: $\Delta S°_{298.15}$, e.u.[b]	$\Delta S°_{298.15}$, e.u., for reaction 7: Experimental	$\Delta S°_{298.15}$, e.u., for reaction 7: Calculated from eq. 6
CH_3	3.71×10^4	9.70	−0.5	19.09	0.00	0.00
Cl	8.89×10^5	9.75	+0.3	28.17	9.1	9.4
Br	9.85×10^5	9.46	0.0	27.41	8.3	9.7
NO_2	3.45×10^9	9.60	−1.5	38.51	19.4	33.9
CN	1.428×10^{16}	9.93	−11.5	35.42	16.3	79.0

[a] Calculated from K at or near 25° given in Table I and the value of ΔH in this table. [b] Calculated using the standard equations for equilibria. See G. N. Lewis and M. Randall ("Thermodynamics," 2nd Ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, Chapter 15) for an example.

Discussion

Form of the Dissociation.—The values of K listed in Table I show no significant change with independently varied concentrations. Hence, the assumed form of the carbinol dissociation, reaction 1, can be considered justified for all Z, except, possibly, Z = CN. The dissociation of 2-cyano-2,2-dinitroethanol proceeds so readily in water that a large excess of formaldehyde and high acid concentrations must be used to obtain an accurate measure of the carbinol concentration. Molar concentrations of HCl greater than 2.37 were avoided because the protonation equilibrium constant for formaldehyde would probably be required.[25a]

Structural Invariance of K/K_i.—Although the values of K (and K_i) given in Table I cover a range of more than 10^{11}, Table II shows that K/K_i is nearly independent of Z at 25°. Similarly, K/K_i at 10° is nearly independent of Z (Z $\neq$ CN). In other words, the equilibrium constant for reaction 5 is nearly independent of Z for water solutions. Further, values of K and K_i are

$$Z(NO_2)_2CCH_2OH + H_2O \rightleftarrows Z(NO_2)_2CH + CH_2(OH)_2 \qquad (5)$$

sufficiently precise to conclude that ΔH for reaction 5 is close to zero for all Z except CN.[25b]

Change of K with Structure.—One can show that the change in K when CH_3 is replaced by Cl or Br is due to a change in the electrostatic energy of the carbanion. Hammett has shown that, for the reaction $A_1^- + HA_2 \rightleftarrows HA_1 + A_2^-$, eq. 6 holds, if, and only if, the change in the

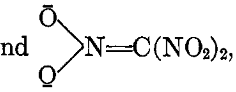
$$\Delta S = -0.005\ \Delta F \text{ (for water solutions at 25°)} \qquad (6)$$

internal energy, ΔE_n, is negligible compared with change in the electrostatic energy of the ions, ΔE_e.[26] Following this treatment, Table II gives, for reaction 7, ΔS and

$$Z(NO_2)_2CCH_2OH + CH_3(NO_2)_2C^- \rightleftarrows Z(NO_2)_2C^- + CH_3(NO_2)_2CCH_2OH \qquad (7)$$

$-0.005\Delta F$, calculated from $K_{298.15}$ and ΔH in Table II. Clearly, the approximation $\Delta E_n << \Delta E_e$ is justified for Z = Cl and Br.[27]

The approximation $\Delta E_n << \Delta E_e$ is not valid for Z = CN and NO_2. An obvious rationalization is that these groups contribute additional structures, such as $\overline{N}{=}C{=}C(NO_2)_2$ and



$>N{=}C(NO_2)_2$

, to the resonance hybrids describing $NC(NO_2)_2C^-$ and $(NO_2)_3C^-$, making these carbanions more stable than $CH_3(NO_2)_2C^-$. Further, the additional resonance stabilization by the third NO_2 group may be less than that provided by the CN group, because repulsion between the oxygen atoms of different nitro groups of $(NO_2)_3C^-$ might be expected to make this carbanion deviate more from coplanarity than $NC(NO_2)_2C^-$.[28] The latter rationalization has been suggested to explain the qualitative observation that nitroform is a much weaker acid than cyanodinitromethane.[8] The anomalously weak acidity of nitroform may explain why the nitromethanes, but not the cyanomethanes, show the "saturation effect" on acidities.[29]

Test of Proposed Correlations.—Leffler has listed many reactions for which $\Delta H/\Delta S$, or $\Delta H^*/\Delta S^*$, is independent of structural and/or solvent changes.[30] However, it was found that reactions which created or destroyed ions, notably carbanion reactions, usually failed to show this invariance. Thus, it is not surprising that $\Delta H/\Delta S$ for reaction 1 is far from independent of Z. In fact, when the approximation $\Delta E_n << \Delta E_e$ is not valid for the structural changes made in an equilibrium reaction, such as eq. 7, then it follows from Hammett's discussion[26] that $\Delta H/\Delta S$ is independent of structural changes only under the rather fortuitous circumstance that $(\Delta E_n + \Delta E_e)$ is proportional to ΔH or ΔS.

Finally, it must be pointed out that the correlation of the ionization constants of a limited series of mono-, di-, and trinitromethanes, $Z_1Z_2Z_3CH$, with the inductive

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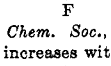
(25) (a) The basicity of formaldehyde has not been measured but is probably similar to that reported for methanol [N. C. Deno and M. J. Wisotsky, *J. Am. Chem. Soc.*, **85**, 1735 (1963)]. (b) This result suggests, but certainly does not prove, that the CN, NO, and CZ bond energies in the methane and its derivative carbinol are (nearly) the same.

(26) L. P. Hammett, "Physical Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 80.

(27) The large positive ΔS for reaction 7 for Cl and Br may be interpreted as follows. The charge of $Cl(NO_2)_2C^-$ and $Br(NO_2)_2C^-$ is more dispersed than that of $CH_3(NO_2)_2C^-$ because Cl and Br are more electronegative (electron withdrawing) than tetrahedral C (see the empirical electronegativities in L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 93); this increased charge dispersal results in a decreased specificity of orientation of the water molecules solvating the halodinitromethide ions.

(28) For the anomalous decrease in the CF bond length of the fluoromethanes with increasing fluorine content (see citation in ref. 27, p. 314), at least two rationalizations have been offered. (i) Double bond–no bond resonance, involving such structures as



$H{-}\overset{\overline{F}}{\underset{F}{C}}{=}\overset{+}{F}$

, increases with increasing fluorine content [J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963)]. (ii) The s-character of *all* carbon orbitals increases with increasing fluorine content, resulting in a progressive shortening and strengthening of the CF bond [D. Peters, *J. Chem. Phys.*, **38**, 561 (1963)]. The highly electronegative nitrogen in the nitro group may behave like fluorine—$(NO_2)_3CCH_2OH$ may be especially stable owing to double bond–no bond resonance, or its C–C bond may be abnormally strong owing to an increase in the s-character of all orbitals of the 2-carbon.

(29) R. G. Pearson and R. D. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953). An accurate value for the pK of cyanoform, −5.1, has been recently reported by Boyd.[28]

(30) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

constant for $Z_1Z_2Z_3C^{-31}$ cannot be extended to include cyanodinitromethane. This correlation predicts that nitroform and cyanodinitromethane should have about the same pK values,[31] while Table I shows that their pK values differ by more than 6!

Summary

The effect of changing Z on the equilibrium constant, K, for the dissociation of the carbinol $Z(NO_2)_2CCH_2OH$ according to eq. 1 can be rationalized in terms of changes in the stability of the carbanion $Z(NO_2)_2C^-$ produced by dissociation of the carbinol. (i) The increase in K when CH_3 is replaced by Cl or Br is due to a change in the electrostatic energy of the carbanion. (ii) The increase in K when CH_3 is replaced by NO_2 or CN is much greater than the change in the electrostatic energy of the carbanion predicts. (iii) Effect ii may be due to the extra resonance stabilization of $(NO_2)_3C^-$ by the third nitro group and of $NC(NO_2)_2C^-$ by the cyano group. The third nitro group may contribute less extra resonance stabilization than the cyano group because O–O repulsion makes the carbanion $(NO_2)_3C^-$ deviate sufficiently from coplanarity to make K for Z = NO_2 much less than for Z = CN.

Acknowledgment.—The author wishes to thank Dr. D. V. Sickman for advice and encouragement, Drs. K. G. Shipp and O. H. Johnson and Messers. F. Taylor, Jr., B. O. Wilkerson, D. W. Jensen, and L. N. Ferguson for samples of the nitroaliphatic compounds used, Dr. H. E. Ruskie for the Russian translations, and Dr. M. Aldridge, American University, Washington, D. C., for the microanalyses.

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[31] V. I. Slovetskii, A. A. Fainzil'berg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 989 (1962). The proposed equation is pK = 12.64 − 2.6 × (inductive constant for $Z_1Z_2Z_3C$). The inductive constant is to be evaluated as Taft's σ^*-value for $Z_1Z_2Z_3C$ or, when this is not available, as $\sum_i (\sigma^* \text{ for } Z_iCH_2)$. For $(NO_2)_3C$, σ^* has been experimentally evaluated as 4.54 [J. Hine and W. C. Bailey, *J. Org. Chem.*, **26**, 2098 (1961)]; the inductive constant for $NC(NO_2)_2C$ can be estimated as 4.10 by the second method, using σ^*-values for $NCCH_2$ and O_2NCH_2 given by Taft (R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 592, 618).

The Reactions of 2,3-Dichloro-1,4-naphthoquinone with Alkali Metal Cyanides

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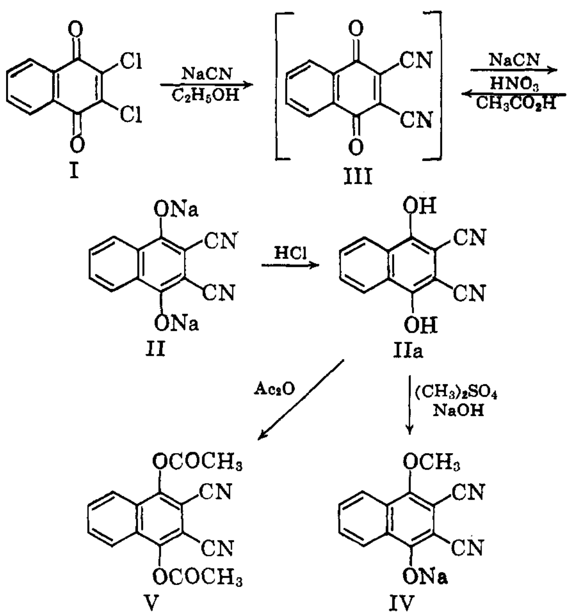
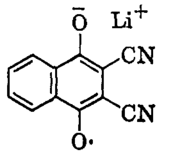
Received May 19, 1964

The product obtained by the reaction of 2,3-dichloro-1,4-naphthoquinone with alkali metal cyanides is shown to be the alkali metal salt of 2,3-dicyano-1,4-naphthalenediol. The probable course of the reaction is investigated.

The reactions of 2,3-dichloro-1,4-naphthoquinone (I) with nucleophilic reagents are well documented, and it seemed unusual that the reaction of I with alkali metal cyanides had not been reported previously. We found that a mixture of I and sodium or potassium cyanide in ethanol, acetonitrile, or dimethylformamide gave a water-soluble product which was found to be the sodium or potassium salt of 2,3-dicyano-1,4-naphthalenediol (II). The initial product formed from I and the cyanide was probably 2,3-dicyano-1,4-naphthoquinone (III) which was then reduced by cyanide to II. This was demonstrated by preparing the quinone III by oxidation of IIa with nitric acid and treating III with aqueous sodium cyanide, which resulted in the immediate solution of III to form the water-soluble II. The nature of this reduction by means of the cyanide ion was not investigated, and it is not known whether this reduction proceeds through an ion radical similar to that formed from tetracyanoethylene with sodium cyanide.[1] The quinone III was reduced to IIa by sodium dithionite. Lithium iodide with III in acetonitrile solution yielded a green monolithium salt which is probably the ion radical VI since an aqueous solution shows a weak e.p.r. absorption. It has been shown[2] that certain quinones can form stable, free-radical salts. The susceptibility of the quinone III to reduction suggested that it might be a useful dehydrogenation agent, but no naphthalene was formed after a benzene solution of tetralin and III had





VI

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[1] O. Webster, W. Mohler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

[2] H. Kainer, D. Bijl, and A. C. Rose-Innes, *Nature*, **178**, 1462 (1956); K. Ley and E. Muller, *Angew. Chem.*, **70**, 469 (1958).