[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Acid Dissociation and Tautomerism of 1,1-Dinitroparaffins

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The acidic properties of 1,1-dinitropropane and 1,1-dinitroethane have been investigated. Values for the apparent ionization constant, $K_{app} = (H^+)(A^-)/[(\text{nitro}) + (\text{aci})]$, the aci ionization constant, $K_{aci} = (H^+)(A^-)/(\text{aci})$, the tautomeric equilibrium constant, $K_i = (\text{aci})/(\text{nitro})$ and the nitro ionization constant, $K_n = (H^+)(A^-)/(\text{nitro})$ have been obtained for both of these dinitroparaffins. The values for 1,1-dinitropropane are $K_{app} = 2.2 \times 10^{-6}$, $K_{aci} = 8 \times 10^{-5}$, $K_i = 5 \times 10^{-2}$ and $K_n = 2.3 \times 10^{-6}$, while the values for 1,1-dinitroethane are, respectively, 5.2×10^{-6}, 1×10^{-4}, 4×10^{-2} and 5.4×10^{-6}.

It has long been known that nitroparaffins that have one or more hydrogen atoms on the α-carbon are weakly acidic. The un-ionized nitroparaffins can and do exist in two tautomeric forms, aci and nitro, each of which is an acid of different strength. The best evidence to date strongly supports the idea that the anion formed by the ionization of the aci form is the same as that obtained from the nitro form.

Turnbull and Maron[1] have determined the ionization constants of aci and nitro forms of some mononitroparaffins and have calculated tautomeric equilibrium constants for several such compounds. Hantzsch[2] has investigated 1,1-dinitroethane conductimetrically and has obtained the apparent acid ionization constant.

The principal purpose of this investigation has been to determine the acid ionization constants for the aci and nitro forms of 1,1-dinitropropane and 1,1-dinitroethane and the tautomeric equilibrium constants.

The various equilibria in question and their equilibrium constants can be formulated as follows where the expressions in parentheses represent the activities or concentrations of the appropriate species.[2,3]

$$\begin{tikzcd} \text{nitro form} \arrow[rr, shift left, "\text{slow}"] \arrow[dr, shift left] \arrow[dr, phantom, "\text{slow}"', shift right=3] & & \text{aci form} \arrow[ll, shift left] \arrow[dl, shift left] \arrow[dl, phantom, "\text{fast}", shift left=3] \\ & H^+ + A^- \arrow[ul, shift left] \arrow[ur, shift left] & \end{tikzcd} \tag{1}$$

$$K_i = (\text{aci form})/(\text{nitro form}) \tag{2}$$

$$K_n = (H^+)(A^-)/(\text{nitro form}) \tag{3}$$

$$K_{aci} = (H^+)(A^-)/(\text{aci form}) \tag{4}$$

If sufficient time is allowed for the system to reach equilibrium, the nitroparaffin will have an apparent acid ionization constant that can be represented by K_{app}. The following useful relations between the various equilibrium constants are easily derived.

$$K_{app} = (H^+)(A^-)/[(\text{nitro form}) + (\text{aci form})] \tag{5}$$

$$K_n = K_i K_{aci} \tag{6}$$

$$K_{app} = K_n/(1 + K_i) \tag{7}$$

Experimental

1,1-Dinitroethane and its potassium salt were prepared by the method of ter Meer.[4,5] His method was modified by the manner in which the nitroparaffin was freed from the crude salt. The crude salt was dissolved in water, the solution cooled to 5° and the calculated amount of 90% formic acid was added dropwise with stirring to give a colorless oil (instead of a blue oil which was obtained with sulfuric acid) which separated and was extracted with ether. Careful distillation of the nitroparaffin gave material which boiled sharply at 80.5° (14 mm.) (reported[6,7] 75-76° (11 mm.)), 55-57° (4 mm.), $n^{25}D$ 1.4322 (reported[6,7] $n^{25}D$ 1.4319, $n^{25}D$ 1.4345)). The compound gave a satisfactory analysis.

The potassium salt of 1,1-dinitroethane used in this work was prepared from the analytically pure material just described by adding dropwise with stirring slightly less than an equivalent amount of potassium hydroxide dissolved in ethanol to an ethanol solution of the 1,1-dinitroethane cooled to 5°. The yellow precipitate was filtered, washed exhaustively with absolute ether and dried in a vacuum desiccator. Its purity as determined by analysis was satisfactory.

1,1-Dinitropropane and its potassium salt were prepared according to the preceding directions. Careful distillation of the nitroparaffin gave material which boiled sharply at 83° (14 mm.) (reported[6] 76-77° (10 mm.)), $n^{25}D$ 1.4320 (reported[6] $n^{25}D$ 1.4316). The compound gave a satisfactory analysis.

The potassium salt of 1,1-dinitropropane was prepared from the analytically pure material just described and the yellow salt gave a satisfactory analysis. In contrast to the 1,1-dinitroethane salt which developed an orange color and a distinctive odor upon standing several days, this salt developed neither color change nor odor over a period of two months.

Procedure.—The apparent ionization constants of 1,1-dinitropropane and 1,1-dinitroethane were determined potentiometrically by means of a Beckman Model G *p*H meter equipped with a calomel reference electrode and a glass electrode. The instrument was calibrated at *p*H 4.01 and 7.00 *vs.* standard buffer solutions purchased from the Fisher Scientific Company. The *p*H measurements were carried out at 25.0 ± 0.2°. Buffer solutions of known concentrations of potassium salt of one of the dinitroparaffins and the dinitroparaffin itself were made up by dissolving weighed samples of the appropriate compounds to form known volumes of solution. Further solutions were sometimes prepared by dilution. Solutions of the dinitroparaffins alone were also prepared in the same fashion. After sufficient time for the system to reach equilibrium was allowed (from 10 to 60 min.) the *p*H of each solution was determined. In the case of dinitropropane buffers the *p*H, once equilibrium was attained, was found to be constant for 30 hours after which time the measurements were discontinued.

The fraction of the aqueous dinitroparaffin in the aci form was determined by bromine titration according to a procedure similar to that used by Conant and Thompson[8] for the investigation of keto-enol equilibria. All of these measurements were carried out in an ice-bath. The 1,1-dinitropropane or 1,1-dinitroethane was dissolved in distilled water and the bromine for the titration was dissolved in methyl alcohol.

For the direct determination of the aci ionization constant, standard solutions of potassium salt of 1,1-dinitropropane were prepared and allowed to come to equilibrium. Measured quantities of standard perchloric acid were rapidly

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[1] D. Turnbull and S. H. Maron, THIS JOURNAL, **65**, 212 (1943). See also G. W. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943).

[2] H. Ley and A. Hantzsch, *Ber.*, **39**, 3149 (1906).

[3] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 634.

[4] E. ter Meer, *Ann.*, **181**, 1 (1876).

[5] The starting material, 1-chloro-1-nitroethane, is not commercially available any longer and an unpublished method of Prof. L. B. Clapp was used to prepare this compound.

[6] L. B. Clapp, unpublished data.

[7] H. Shechter and L. Zeldin, THIS JOURNAL, **73**, 1276 (1951).

[8] J. B. Conant and A. F. Thompson, *ibid.*, **54**, 4039 (1932).

added to the stirred salt solutions and the time recorded. The pH was then measured at various times and extrapolated back to an initial pH value. The observed increase of pH with time is due to the isomerization of the liberated aci acid and subsequent removal of hydrogen ions from the solution by dinitropropane anions. This procedure for the determination of the aci constants is similar to that successfully used by Turnbull and Maron[1] in their investigation of aci ionization of mononitroparaffins.

Results

In Table I the results of the determination of apparent ionization constants for 1,1-dinitroethane and 1,1-dinitropropane are given.

TABLE I

DETERMINATION OF K_{app} OF 1,1-DINITROETHANE AND 1,1-DINITROPROPANE AT 25°

$(HA)_{total} \times 10^3$	$(KA) \times 10^4$	$(H^+) \times 10^5$	$K_{app} \times 10^6$
	1,1-Dinitroethane		
22.30	0	31.6	5.2
12.97	30.38	2.10	4.9
2.23	1.384	0.86	5.4
0.892	0	6.31	4.8
9.838	20.54	2.57	5.4
2.590	6.08	2.10	5.1
0.984	20.54	2.24	5.3
Av. $K_{app} = 5.2 \times 10^{-6}$		Av. dev. $= 0.2 \times 10^{-6}$	
	1,1-dinitropropane		
Av. $K_{app} = 2.2 \times 10^{-6}$		Av. dev. $= 0.2 \times 10^{-6}$	

Data for the bromine titration experiments which were carried out to determine the fraction of 1,1-dinitropropane and 1,1-dinitroethane in the aci form are given in Table II. From a consideration of the magnitude of the possible error in the titration end-point and the error introduced by the slight hydrolysis of bromine we estimate that the maximum uncertainty in K_i is about twice the average deviation.

TABLE II

DATA FOR BROMINE TITRATION OF 1,1-DINITROPROPANE AT 0°

Moles dinitropropane $\times 10^3$	Moles $Br_2 \times 10^5$	$K_i \times 10^2$
1.82	6.0	3.4
3.03	1.7	0.6
0.57	2.0	3.6
0.98	6.0	6.5
0.73	5.2	7.6
0.33	1.9	6.1
Av. $K_i = 5 \times 10^{-2}$	Av. dev. $= 2 \times 10^{-2}$	
BROMINE TITRATION OF 1,1-DINITROETHANE AT 0°		
Av. $K_i = 4 \times 10^{-2}$	Av. dev. $= 1 \times 10^{-2}$	

Data from a typical experiment for the determination of the aci ionization constant of 1,1-dinitropropane are given in Table III. The extrapolation to initial pH is of necessity rather arbitrary and leads to some uncertainty in the calculated values of K_{aci}. The average of six such experiments gave a value of 8×10^{-5} for K_{aci}. The average deviation from this value is 5×10^{-5} and our estimate of the probable uncertainty is about 20% larger than the average deviation.

TABLE III

DIRECT DETERMINATION OF K_{aci} FOR 1,1-DINITROPROPANE AT 25°

moles/l. $KC_3H_5(NO_2)_2 = 4.3 \times 10^{-3}$
moles/l. H^+ added $= 3.7 \times 10^{-4}$

Time, sec.	pH	
0	5.2 (extrapolated)	
14	5.76	
30	6.19	$K_{aci} = 6.8 \times 10^{-5}$
40	6.26	
75	6.49	
180	6.50	

It is possible to obtain an internal check on the various equilibrium constants that have been determined for 1,1-dinitropropane by calculating K_n from equation 6 and also from equation 7. The values so obtained are in satisfactory agreement and we shall take $K_n = 2.3 \times 10^{-6}$ as calculated from 7.

A summary of best values for the various equilibrium constants we have obtained and a short compilation of values from the literature for some other acids are given in Table IV.

Discussions and Conclusions

K_i values for the 1,1-dinitroparaffins indicate the presence of approximately 4% aci form in the tautomeric mixtures. This is a considerably larger aci content than is indicated for the mononitroparaffins and would be expected in view of the presence of the second nitro group.

As can be seen from Table IV, K_n values are larger for dinitroparaffins than for the mononitroparaffins. The electronegativity of the nitro substituent in the latter produces this marked difference and the magnitude of the effect, approximately a thousand-fold, is comparable to that in acetic acid and nitroacetic acid. K_{aci} values follow no such regular trend; in fact, they are not very different from all of the compounds listed. It is possible that the aci forms of the dinitroparaffins

TABLE IV

EQUILIBRIUM CONSTANTS FOR NITROPARAFFINS AND RELATED ACIDS

	K_{app}	K_i	K_{aci}	K_n
1,1-Dinitroethane	5.2×10^{-6}	4×10^{-2}	1×10^{-4}	5.4×10^{-6}
1,1-Dinitropropane	2.2×10^{-6}	5×10^{-2}	8×10^{-5}	2.3×10^{-6}
Nitromethane[1]	6.1×10^{-11}	1.1×10^{-7}	5.6×10^{-4}	6.1×10^{-11}
Nitroethane[1]	3.5×10^{-9}	8.9×10^{-5}	3.9×10^{-5}	3.5×10^{-9}
Nitropropane[1]	1.0×10^{-9}			
2-Nitropropane[1]	2.1×10^{-8}	2.75×10^{-3}	7.7×10^{-6}	2.1×10^{-8}
Acetic acid	1.8×10^{-5}			
Chloroacetic acid	1.52×10^{-3}			
Nitroacetic acid[9]	2.09×10^{-2}			

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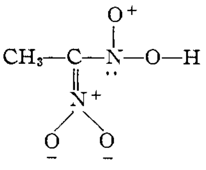
[9] K. J. Pederson, *J. Phys. Chem.*, **38**, 559 (1934).

are not appreciably stronger acids than the acid



$CH_3-\underset{\underset{O^-\ \ O^-}{N^+}}{\overset{\|}{C}}-\overset{O^+}{\overset{|}{\ddot{N}}}-O-H$

forms of the mononitroparaffins because one of the dinitroparaffin resonance forms shows an increased electron density on nitrogen. This would tend to counterbalance the electronegative effect of the second nitro group. At any rate the considerable variation in K_{app} values for nitroparaffins is almost entirely due to differences in the acid strengths of the nitro forms.

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[CONTRIBUTION FROM THE QUARTERMASTER RESEARCH & DEVELOPMENT CENTER]

Spectroscopic Studies on Dyes. II. The Structure of N,N'-Dimethylindigo[1]

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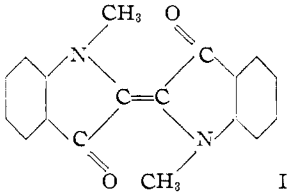
In contrast with other indigo dyes, N,N'-dimethylindigo is a low-melting green compound which is very soluble in organic solvents and has little affinity for cellulosic fibers. The wave length of the visible absorption band of this dye is strongly dependent on the nature of the solvent; hydroxylic solvents, in particular, cause a strong bathochromic shift. The absorption band shifts to still longer wave lengths in the solid phase. Rapid *trans* to *cis* isomerization occurs when a solution of this dye is irradiated with yellow or red light; reversal of the reaction in the dark is almost instantaneous. The compound also forms hydrogen-bonded complexes with phenol and ethanol. These observations suggest that, probably due to the steric effect of the methyl groups, the central double bond of this compound has considerably more single-bond character than in other indigo or thioindigo dyes.

Introduction

When in 1912 Ettinger and Friedlaender first described N,N'-dimethylindigo (I),[2] they observed



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that this dye possessed some rather unexpected properties. They found the contrast between N,N'-dimethylindigo and indigo to be particularly striking; the principal differences noted by these investigators are tabulated in Table I. It is clear from this tabulation that the extent of these differences far exceeds that which might normally be expected to result from the replacement of two hydrogen atoms by methyl groups.

TABLE I

PHYSICAL PROPERTIES OF N,N'-DIMETHYLINDIGO

	N, N'-Dimethylindigo	Indigo
M.p., °C.	182°	>300°
Solubility in common organic solvents	Very soluble	Almost completely insoluble
$\lambda_{\max}$ (in xylene), mμ	644.5	591
Color	Green	Blue
Behavior toward hot aq. bases	Rapid dec.	No reaction
Behavior toward aq. mineral acids	Forms soluble salts	No reaction
Affinity of leuco-form for cotton	Almost none	Good

Since recent investigations, using modern physical techniques, have shed much light on the structure of other indigo dyes,[3] a spectroscopic study of this dye was undertaken in the hope of arriving at a better understanding of its unusual properties. Moreover, it was believed that the results of such a study would constitute an important addition to the over-all picture of the structure, configuration and behavior of dyes containing a central double bond (*e.g.*, indigo,[3] thioindigo[4] and azo dyes).[5]

Experimental

(A) Preparation of N,N'-Dimethylindigo.—The dye was prepared from N-methylanthranilic acid (Eastman Kodak Co.; reagent grade) by the procedure (1) of Ettinger and Friedlaender.[2] The dye was obtained in essentially pure form, m.p. 181–182° (reported[2] 182°).

(B) Measurement of the Spectra.—Spectra in the visible and ultraviolet regions were determined by means of a Cary Model 11 Spectrophotometer. For measurements on solutions the solvent was used as the reference, utilizing matched fused quartz absorption cells. The spectra were also determined in the solid phase by the KBr-pellet technique.[6] In addition, measurements were made in the visible region on a solution of this dye in benzene, using an American Optical Co. (AO) Rapid-Scanning Spectrophotometer. A Beckman IR-3 Spectrophotometer equipped with NaCl or LiF optics, as appropriate, was used for measurements in the infrared region. Infrared spectra were determined in solutions in CCl_4 (against the solvent as reference), on a mull in Nujol (against Nujol), and on a pellet mixed with KBr (against KBr).

(C) Photochemical *trans*→*cis* Isomerization.—The photochemical isomerization of this dye was studied using both the Cary and AO instruments. Exploratory experi-

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(1) Presented before the Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March, 1956, Pittsburgh, Pennsylvania.

(2) L. Ettinger and P. Friedlaender, *Ber.*, **45**, 2074 (1912).

(3) (a) W. R. Brode, E. G. Pearson and G. M. Wyman, THIS JOURNAL, **76**, 1034 (1954); (b) J. Weinstein and G. M. Wyman, *ibid.*, **78**, 2387 (1956); (c) H. v. Eller, *Compt. rend.*, **239**, 975 (1954); (d) E. A. Gribova, *Compt. rend. Acad. Sci. USSR*, **102**, 279 (1955).

(4) (a) G. M. Wyman and W. R. Brode, THIS JOURNAL, **73**, 1487 (1951); (b) W. R. Brode and G. M. Wyman, *J. Research Natl. Bur. Standards*, **47**, 170 (1951); (c) W. R. Brode and G. M. Wyman, THIS JOURNAL, **73**, 4267 (1951).

(5) (a) W. R. Brode, J. H. Gould and G. M. Wyman, *ibid.*, **74**, 4641 (1952); (b) **75**, 1856 (1953); (c) W. R. Brode, I. L. Seldin, P. E. Spoerri and G. M. Wyman, *ibid.*, **77**, 2762 (1955).

(6) G. M. Wyman, *J. Opt. Soc. Amer.*, **45**, 965 (1955).