was 98%. The pure crystals were obtained from ethanol, m.p. 164–165°.

Anal. Calcd. for $C_{18}H_{16}O_2SSi$: Si, 9.73. Found: Si, 9.60.

Cleavage by Hydrogen Chloride.[1,8]—Hydrogen chloride was allowed to pass for 15 hours through a refluxing solution of 0.01 to 0.02 mole of organosilicon compound in glacial acetic acid (50 to 100 ml.) and successively through a small ground glass trap immersed in- a Dry Ice–acetone-bath. After cooling, the solution was poured into water and the solid which separated removed by filtration. When cleavage took place, the liquid in the trap was purified by two distillations and was shown to be trimethylsilyl chloride. The reagent used for characterizing the trimethylsilyl chloride was 9-fluorenyllithium. The product[9] formed in this manner was shown to be 9-trimethylsilylfluorene (m.p. and mixed m.p. 97–99°). The yields of dibenzothiophene from the cleavage of (II) and (III) were 99 and 97%, respectively. The percentage recoveries of dioxide from the attempted cleavages of (V) and (VI) were 94 and 97%, respectively.

Acknowledgment.—One of us (G. I.) wishes to express his appreciation to the Institute of International Education and to the Research Council of Iowa State College for fellowship aid.

(8) See H. Gilman and F. J. Marshall, THIS JOURNAL, 71, 2066 (1949), for earlier cleavage studies by this procedure.

(9) Unpublished studies by R. A. Benkeser.

The Mechanism of Cellulose Nitration[1]

BY RALPH KLEIN AND MORRIS MENTSER

The mechanism of nitration of aromatic molecules by mixed acid has been established by rate studies[2,3,4] which show that nitration is effected by the NO_2^+ ion. Physical and chemical evidence has established the presence of this ion in the concentrated mixed acid used in nitration reactions.[5] Since cellulose is nitrated most effectively in the acid concentration region in which the NO_2^+ ion is found to exist, by analogy it might be expected that nitration of cellulose occurs *via* an electrophilic attack on the hydroxyl oxygen by the NO_2^+ ion with proton elimination. Indeed, such a mechanism has been postulated for nitration of starches.[6] It is evident that, if this mechanism is operative, cellulose nitrate prepared from ordinary cellulose and O^{18}-enriched mixed acid should have nitrate groups in which only two of the three nitrate oxygens are O^{18}-enriched. This is confirmed by the present experiments. It may be concluded that the oxygen of the alcohol groups of the cellulose is not eliminated in the nitration reaction and thus remains unenriched. An analogous result has been obtained from studies of the esterification of methyl alcohol with benzoic acid.[7]

(1) Publication approved by the Office of Public Information, U. S. Department of Defense. Not copyrighted.

(2) F. H. Westheimer and M. S. Kharasch, THIS JOURNAL, 68, 1871 (1946).

(3) A. M. Lowen, M. A. Murray and G. Williams, J. Chem. Soc., 3318 (1950).

(4) R. J. Gillespie, E. D. Hughes, C. K. Ingold, D. J. Millen and R. I. Reed, Nature, 163, 599 (1949).

(5) G. M. Bennett, J. C. D. Brand and G. Williams, J. Chem. Soc., 869 (1946).

(6) S. Israelashvili, Nature, 165, 686 (1950).

(7) I. Roberts and H. C. Urey, THIS JOURNAL, 60, 2391 (1938).

Experimental

Samples of O^{18}-enriched cellulose nitrate were prepared by nitration of cotton linters with an O^{18}-enriched sulfuric acid–nitric acid–water mixture. Since both nitric acid and sulfuric acid exchange oxygen with water,[8,9] the admixture of heavy water to ordinary acids provides a convenient method for preparing the enriched acids. The O^{18}-enrichment factor was determined by mass spectrometer analysis of the NO resulting from a nitrometer reaction with the mixed nitrating acid.

The cellulose nitrate was analyzed for O^{18} by the method of von Grosse, *et al.*[10] The samples were heated at 750° for 1.5 hours in a quartz bulb. Under such conditions, oxygen randomization occurs among the decomposition products, and the enrichment factor could be determined by an O^{18} analysis of the CO_2 formed. The results are shown in Table I. Experiment 1(b) shows that, at the temperatures and times involved in these experiments, oxygen exchange with the quartz is negligible.

TABLE I

ENRICHMENT FACTORS FOR EQUILIBRATED DECOMPOSITION PRODUCTS OF O^{18}-ENRICHED CELLULOSE NITRATE

Expt.	Heating time, hours	Nitrogen content, %	O^{18}-Enrichment factor of nitrating acid	3 Enriched O-atoms in NO_3 group	2 Enriched O-atoms in NO_3 group	Exptl.
1(a)	1.5	11.1	4.9	3.6	2.7	2.2
1(b)[a]	3.0	..	...	...	...	2.2
2	1.5	11.1	4.9	3.6	2.7	2.6
3	1.5	11.1	4.9	3.6	2.7	2.7
4	1.5	8.7	5.7	3.5	2.7	2.6

[a] Same gas sample as (a) but heated 1.5 hours longer.

The number of nitrate groups per glucose unit was determined from nitrogen analysis. It was thus possible to calculate the enrichment factor resulting from oxygen randomization of the total oxygen of the cellulose nitrate molecule, assuming that either three or two of the three nitrate oxygens were enriched. These values are given in columns 4 and 5 of Table I. Except for the slightly low result of experiment 1, which may be attributed to incomplete preliminary outgassing of the quartz bulb, the experimental results of column 6 agree with column 5. This shows that the oxygen of the hydroxyl groups is not eliminated in the nitration reaction.

The authors express their appreciation to Dr. R. A. Friedel for the mass spectrometer isotope analyses.

(8) R. Klein and R. A. Friedel, ibid., 72, 3810 (1950).

(9) E. R. S. Winter, M. Carlton and H. V. A. Briscoe, J. Chem. Soc., 131 (1940).

(10) A. V. Grosse, S. G. Hindin and A. D. Kirshenbaum, Anal. Chem., 21, 386 (1949).

A New Preparation of 2,4-Dinitrophenylhydrazones

BY G. DANA JOHNSON

A phosphoric acid–ethanol solution of 2,4-dinitrophenylhydrazine has been found to be indefinitely stable and avoids the use of the more reactive sulfuric acid.

Reagent.—To make one liter of approximately 0.25 M reagent, 50 g. of 2,4-dinitrophenylhydrazine was dissolved in 600 ml. of 85% phosphoric acid in a one-liter beaker on a steam-bath. The solution was diluted with 395 ml. of 95% alcohol and clarified by suction filtration through a thin layer of Filter-Cel.

Use.—To a solution of the carbonyl compound in alcohol was added the calculated volume of reagent. Amino car-

bonyl compounds reacted with the reagent to form yellow or red solutions or, in some cases, a yellow precipitate. Dilution with water caused the deposition of the normal deep red or black D.N.P.

Table I lists twenty-five new 2,4-dinitrophenylhydrazones in order of the increasing depth of color. All melting points are corrected.

TABLE I

2,4-Dinitrophenyl-hydrazone of	Color	M.p., °C.	Analyses, % Nitrogen Calcd.	Found[a]
Methyl acetoacetate	Yellow	119.0–119.5	18.91	19.21
m-Nitroacetophenone	Orange	232.5–233.0	20.29	20.26
β-Benzoylacrylic acid	Orange	229.0–229.5	15.73	15.88
2-Hydroxy-5-methyl-benzophenone	Orange	244.5–245.0	14.28	14.37
α-Bromoacetophenone	Orange	220.0–220.5	14.78	14.76
p,α-Dibromoaceto-phenone	Orange	218–219	12.23	12.14
p-Isopropylaceto-phenone[b]	Orange	182.0–182.5	16.37	16.48
2-Hydroxybenzophenone	Red-orange	250–251	14.81	14.83
m-Tolualdehyde	Red-orange	193.5–195.5	18.66	18.78
3,3'-Diisopropoxyanisil[b]	Red-orange	186.0–186.5	9.89	10.19
o-Hydroxyacetophenone	Red-orange	213–214	17.72	17.95
4-Phenyl-2-butanone[b]	Red-orange	128.5–129.0	17.07	17.19
α-Bromo-p-phenylaceto-phenone	Red-orange	228.5–229.0	12.31	12.57
p-Phenylacetophenone	Red-orange	241.5–242.0	14.89	15.04
2-Hydroxy-5-methyl-acetophenone	Red	273.0–273.5	16.96	17.26
Methyl 2-thienyl ketone	Red	243–244	18.29	18.29
3,4-Dihydro-1(2H)-naphthalenone	Red	262–263	17.17	17.14
2,3-Diphenyl-1-indanone[c]	Red	245.5–246.5	12.06	12.20
2,4-Dimethoxybenzaldehyde	Red	257–258	16.18	15.88
3-Benzyloxy-4-methoxy-benzaldehyde[b]	Red	196–197	13.27	13.00
3,4-Diethoxybenzalde-hyde	Red	219–220	14.97	14.82
1,7-Diphenyl-1,4,6-hep-tatrien-3-one[d]	Red	179–180	12.72	12.89
3,4-Dimethoxypropio-phenone[b]	Violet-red	178.5–179.0	14.97	15.24
4,4-Bis-(dimethylamino)-benzophenone	Violet-red	273.0–273.5	18.74	18.81
p-Diethylaminobenz-aldehyde	Purple-black	206.5–207.0	19.60	19.68

[a] The analyses were performed by Mrs. Alma Rosen. [b] The carbonyl compound was kindly furnished by Dr. E. E. Campaigne of this Laboratory. [c] The carbonyl compound was kindly furnished by Dr. J. H. Billman of this Laboratory. [d] This ketone was synthesized by the procedure of A. Rosenheim and W. Levy, Ber., 37, 3662 (1904).

CHEMISTRY DEPARTMENT
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA   RECEIVED AUGUST 31, 1951

Hydrogen Bonding and Ionization of Carboxylic Acids in Aqueous Solutions

BY A. KATCHALSKY, H. EISENBERG AND S. LIFSON

The careful determinations of the ionization constant of acetic acid by MacInnes and Shedlovsky[1] and of a series of other carboxylic acids by Saxton and Darken[2] have proved that the limiting Debye–Hückel activity coefficient suffices only at extremely low concentrations of the acids. At slightly higher concentrations at which Debye's approximation should still hold the calculated thermodynamic ionization constants show pro-

(1) D. A. MacInnes and Th. Shedlovsky, THIS JOURNAL, 54, 1429 (1932).
(2) B. Saxton and L. S. Darken, ibid., 62, 846 (1940).

nounced deviations from the extrapolated value; these deviations are larger than would be deduced from the change in the dielectric constant and were attributed by Owen[3] to the "medium effect" of the non-ionized acetic acid molecules on the ionization of the acid. Saxton and Darken[2] found that the dependence of the apparent ionization constant of all the carboxylic acids investigated by them could be described to a very good approximation by the empirical equation

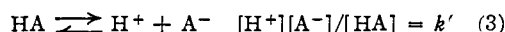$$\log k - 1.013\sqrt{\alpha c} = \log K - B(1 - \alpha)c \quad (1)$$

where k is the classical ionization constant, K the thermodynamic ionization constant, c the concentration of the acid in moles/liter, α its degree of ionization and $1.013\sqrt{\alpha c}$ the Debye–Hückel term, while B is the empirical constant correlating the classical ionization constant with the concentration of non-ionized acid $[(1 - \alpha)c]$.

As will be shown below, this apparently anomalous behavior of carboxylic acids may be ascribed to dimerization of the acids in aqueous solution and the values of the constant B may be derived from the known dimerization constants. Conversely, a knowledge of B presents a new and clear-cut method for the evaluation of the dimerization constant of carboxylic acids. The partial association of carboxylic acids to dimers in aqueous solutions has been established by a variety of experimental investigations, such as cryoscopic data,[4,5] Raman spectra[6] and vapor pressure measurements.[7] The latter method is the only quantitative, thermodynamically justified procedure recorded in the literature for the determination of the dimerization constant of acetic acid. MacDougall and Blumer found the constant to be (0.185 ± 0.011) at 25°; this value will be applied in our calculations.

Our major assumption is that the cyclic dimer[7] has a negligible degree of ionization compared to the unassociated monomer. The state of the solution is then governed by two equilibria

$$2HA \rightleftharpoons H_2A_2 \quad [H_2A_2]/[HA]^2 = L \quad (2)$$

where L is the dimerization constant

$$HA \rightleftharpoons H^+ + A^- \quad [H^+][A^-]/[HA] = k' \quad (3)$$

where k' is the apparent ionization constant, and the quantities in square brackets denote concentrations. The concentration c of the acid is given by

$$c = [A^-] + [HA] + 2[H_2A_2] \quad (4)$$

It is at once evident that the calculation of the ionization constants assuming $[HA] = c - [A^-]$ will lead to erroneous results whenever dimerization is appreciable. Denoting $[A^-]/c = \alpha$ the degree of ionization, a simple calculation leads to the expression

$$k' = [\alpha^2 c/(1 - \alpha)] \cdot \tfrac{1}{2} \cdot [\sqrt{1 + 8L(1 - \alpha)c} + 1] \quad (5)$$

At sufficiently small concentrations, Eq. (5) is approximated by

$$k' = [\alpha^2 c/(1 - \alpha)] \cdot [1 + 2L(1 - \alpha)c] \quad (6)$$

The quantity $\alpha^2 c/(1 - \alpha)$ represents the classical ionization constant k which does not consider dimerization. Hence

$$k' = k[1 + 2L(1 - \alpha)c] \quad (6a)$$

(3) B. B. Owen, ibid., 54, 1758 (1932).
(4) W. A. Roth, Z. physik. Chem., 43, 539 (1903).
(5) E. R. Jones and C. R. Bury, Phil. Mag., [7] 4, 841 (1927).
(6) P. Koteswaram, J. Chem. Phys., 7, 88 (1939); Z. Physik, 110, 118 (1938); ibid., 112, 395 (1939).
(7) F. H. MacDougall and D. R. Blumer, THIS JOURNAL, 55, 2236 (1933).