785. *Nitration of Alcohols at Oxygen Centres. Part II.*[1] *The Equilibria established in Aqueous Sulphuric and Perchloric Acids and the Mechanism of Hydrolysis of the Nitrate Ester.*

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The extent of conversion of 2,4-dinitrobenzyl alcohol into its nitrate and sulphate esters in *O*-nitration experiments in a wide range of sulphuric acid–water mixtures has been measured. Similar experiments with isopentyl alcohol have indicated a mechanism for the hydrolysis of isopentyl nitrate in both aqueous sulphuric and perchloric acid. A relationship between the equilibrium constant, K_N, for *O*-nitration and functions which are a measure of the acidity of the media is deduced and tested.

THE conversion of alcohols into their nitrate esters in high yields can frequently be accomplished by means of nitric acid–sulphuric acid–water mixtures.[2] Numerous studies on hydroxy-compounds have demonstrated both the influence of solvent composition on the yield of nitrate ester and the occurrence of the oxidation and sulphation side reactions.[3] The sulphation in the absence of nitric acid has recently been the subject of a detailed kinetic study in which 2,4-dinitrobenzyl alcohol and ethyl alcohol have been employed.[4] 2,4-Dinitrobenzyl alcohol was suitable for *O*-nitration since unlike ethyl alcohol it was completely resistant to oxidation in the mixed acid. Preliminary experiments on the composition of the equilibrium mixture formed by 0·1M initial concentrations of the alcohol and nitric acid in the range 79—93% sulphuric acid showed that the amount of alcohol consumed was only slightly greater than that converted into the sulphate ester.[4] It was therefore necessary to determine the nitrate ester independently and this was achieved by first oxidising the unchanged alcohol quantitatively with acidic dichromate [3] and then extracting the nitrate ester with an organic solvent for analysis. The concentration of the nitrate ester was thus determined directly and the sulphate ester was obtained by difference from the total 2,4-dinitrobenzyl alcohol consumed. Analyses of reaction mixtures showed that the rates of *O*-nitration were too fast for measurement even at 0° in 70% sulphuric acid and at lower acidities than this the yield of nitrate ester was negligible unless the nitric acid was present in considerable excess over the alcohol. Results at 0° for the range 55—93% sulphuric acid are given in Table 1. These show that with equimolecular initial concentrations of the alcohol and nitric acid in the more concentrated sulphuric acids the nitrate ester is initially formed much more rapidly than the sulphate ester but the latter is finally in large excess in the equilibrium mixture. The nitronium ion is clearly much more reactive than the sulphating entity but the *O*-nitration is reversed as the alcohol is gradually solvolysed; in addition, there may be direct conversion of the nitrate into sulphate ester. Attempts to follow the rate of hydrolysis of the nitrate failed because of the considerable time required for dissolution of the ester in all media except the most strongly acidic where reaction was too fast for measurement. The few analyses of mixtures obtained by starting with nitrate ester are included in Table 1 and they confirm the ultimate predominance of the sulphate ester.

The result of these investigations suggested that a larger proportion of nitrate ester might result even in the stronger acids if a higher initial concentration of nitric acid relative to the alcohol was used for all experiments at 25°; therefore a threefold excess of nitric acid was used. The composition of these equilibrium mixtures are expressed in terms of the equilibrium constants K_N and K_S for nitration and sulphation respectively. K_S, as

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[1] Part I, preceding paper.

[2] Boschan, Merrow, and van Dolah, *Chem. Rev.*, 1955, **55**, 485.

[3] Farmer, *J. Soc. Chem. Ind.*, 1931, **50**, 75T; Chedin, Tribot, and Feneant, *Mém. Services chim. Etat*, 1948, **34**, 277; Rinkenbach and Aaronson, *Ind. Eng. Chem.*, 1931, **23**, 160; Aubertin, *Mém. Poudres*, 1948, **30**, 7; Ohman, *Svensk. kem. Tidskr.*, 1944, **56**, 328.

[4] Williams and Clark, (*a*) *J.*, 1956, 1304; (*b*) *J.*, 1957, 4218.

TABLE 1. O-*Nitration and sulphation of* 2,4-*dinitrobenzyl alcohol at* 0°.

%H_2SO_4	[HNO_3] (M)	[Alcohol] (M)	[Nitrate ester] (M)	Time (min.)	Nitrate ester (%)	Sulphate ester (%)
93	0·1	0·1	—	7	3·7	86
				240	4·1	85
87	0·1	0·1	—	6	19	43
				180	4	80
73	0·1	0·1	—	7	7	3
				240	8	8
70	0·1	0·1	—	7	6	1
				240	5	4
65	0·1	0·1	—	7	0	0
				240	2	0
65	2·0	0·08	—	4	2	—
				30	17	—
				120	17	—
65	4·0	0·1	—	45	55	—
				75	60	—
55	4·0	0·1	—	20	23	—
				35	34	—
				50	43	—
87	—	—	0·1	6	10	74
				180	9	78
77	—	—	0·1	100	9·7	18
75	—	—	0·1	210	5·6	25

previously defined,[4] is represented by (1) and K_N by (2), in which the bracketed quantities represent the experimentally determined concentrations at equilibrium. The constancy

$$K_S = [RSO_4]/[ROH] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$K_N = [RO{\cdot}NO_2]/[ROH][HNO_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

during several hours of the equilibrium composition once attained and the reproducibility of the analytical measurements are shown by the typical set of results for two duplicated experiments recorded in Table 2*a*. Errors in the alcohol and nitrate determinations are magnified in calculating K, but the largest difference between duplicate values of the latter is not more than 5%. Results for the range 75—85% sulphuric acid at 25° are given in Table 2*b*. The falling K_S and K_N values with decreasing acidity reflect the lower yields of both esters. The variation of K_S with composition of the medium in fact is in excellent accord with that obtained in the same range of media in the absence of nitric acid by Williams and Clark.[4]

TABLE 2. O-*Nitration and sulphation of* 2,4-*dinitrobenzyl alcohol at* 25°.

(*a*) Analyses of equilibrium mixtures in duplicate experiments in 80·7% H_2SO_3.
Initial concns.: [Alcohol] = 0·100M; [HNO_3] = 0·318M.

Time (hr.)	10^2 [Alcohol] (M)		10^2 [Nitrate ester] (M)		10^2 [Sulphate ester] (M)		K_N		K_S	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1	4·00	4·07	2·03	2·01	3·97	3·92	1·71	1·66	0·99	0·96
2	4·07	4·10	2·01	2·02	3·92	3·88	1·66	1·66	0·96	0·95
3	4·11	4·11	2·05	2·01	3·84	3·88	1·68	1·64	0·94	0·95
4	4·03	4·03	2·01	2·04	3·96	3·93	1·67	1·76	0·98	0·97

K_N (mean) = 1·67; K_S (mean) = 0·96.

(*b*) Variation of K_N and K_S with composition of the medium. Initial concns.: [Alcohol] = 0·100M; [HNO_3] = 0·300M.

H_2SO_4%	84·9	82·5	80·7	78·6	76·8	74·6
K_N	2·87	2·08	1·67	1·23	0·95	0·71
K_S	2·22	1·41	0·96	0·76	0·55	0·46
$\log K_N - H_0 + C_0$...	−7·39	−7·23	−7·13	−7·10	−6·92	−6·75

Acid Hydrolysis of Nitrate Ester.—It is reasonable to assume that in either reverse reaction, the hydrolysis of the ester if it could be measured directly would be of the first order with respect to the ester. If, for nitration, the rate constants of the esterification reaction and the hydrolysis are k_2 and k_1 respectively, then at equilibrium

$$k_2[\mathrm{ROH}][\mathrm{HNO_3}] = k_1[\mathrm{RO{\cdot}NO_2}] \quad . \; . \; . \; . \; . \; . \quad (3)$$

and hence

$$k_1 = k_2/K_\mathrm{N} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

It was possible to measure K_N only for 2,4-dinitrobenzyl alcohol in these media and not k_2. For isopentyl alcohol however rates of esterification were measurable at 25° both in sulphuric acid and in perchloric acid solutions.[1] Isopentyl nitrate, like 2,4-dinitrobenzyl nitrate, dissolved too slowly in media in which rates of hydrolysis would have been measurable, and k_1 could not be determined directly. Calculated values of k_1 were however obtained from eqn. (4) and are recorded in Table 3. In the strongest acid employed, 75% sulphuric acid, equilibrium was attained in 15 minutes and during this time sulphation of isopentyl alcohol is negligible.

TABLE 3. O-*Nitration of isopentyl alcohol* (k_2) *and hydrolysis of isopentyl nitrate* (k_1) *at* 25°.

(*a*) In perchloric acid

$\mathrm{HClO_4}$%	10^2k_2	K_N	$k_1 = k_2/K_\mathrm{N}$	$\log K_\mathrm{N} - H_0 - \log([\mathrm{Z^+}]/[\mathrm{ZOH}])$
62·0	157	10·0	0·157	4·29
60·8	71	7·39	0·096	4·27
59·3	27	5·93	0·0457	4·33
58·0	10·1	4·10	0·0246	4·31
56·3	5·0	3·24	0·0155	4·39
55·2	2·23	2·43	0·0092	4·38

(*b*) In sulphuric acid

$\mathrm{H_2SO_4}$%	10^2k_2	K_N	$k_1 = k_2/K_\mathrm{N}$	$\log K_\mathrm{N} - H_0 + C_0$
67·0	31·5	19·5	0·0162	−4·28
66·0	25·2	22·4	0·0113	−4·07
65·3	21·9	20·2	0·0108	−4·01
63·5	9·4	13·5	0·0070	−3·97
62·4	5·04	8·3	0·0061	−4·00
60·0	1·72	5·6	0·0031	−3·87
57·7	0·73	3·71	0·0020	−3·73

The calculated values of k_1 show that in both sulphuric and perchloric acid the rate of hydrolysis of isopentyl nitrate increased with acidity but only about half as rapidly as the forward esterification. Since the rate constant of esterification shows an approximate parallelism[4] with the acidity function, C_0, which increases about twice as rapidly as the Hammett acidity function, H_0, with increasing acid strength of the medium the possibility of a direct dependence of the hydrolysis rate constant on H_0 was evident. This was tested by plotting values of log k_1 at 25° against H_0 for both acids. Fig. 1 shows that reasonably good straight-line plots are obtained; the gradients of −0·92 for perchloric acid and of −0·85 for sulphuric acid are sufficiently close to unity to suggest that hydrolysis proceeds through the protonated nitrate ester formed in fractionally small amount.[5] This result also implies that the transition state involves only the protonated ester and does not include a molecule of water.[6] Protonation of a nitrate ester followed by release of a nitronium (nitryl) ion appears to occur in the concentrated acid since such solutions are nitrating media and in pure sulphuric acid there is cryoscopic evidence[7] of the production of five entities per molecule of added nitrate ester which can be represented by equations (5) and (6).

$$\mathrm{RO{\cdot}NO_2 + H_2SO_4 \rightleftharpoons ROH + NO_2^+ + HSO_4^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\mathrm{ROH + 2H_2SO_4 \rightleftharpoons RO{\cdot}SO_3H + H_3O^+ + HSO_4^-} \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

[5] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

[6] Zucker and Hammett, *ibid.*, 1939, **61**, 2779, 2785; Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[7] Kuhn, *J. Amer. Chem. Soc.*, 1947, **69**, 1974.

In aqueous ethanol it has been reported that the hydrolysis of nitrate esters is not catalysed by acids[8] and this is attributed to the loss of resonance stabilisation which would result from protonation of the nitrate group. The hydrolysis of methyl nitrate in aqueous solution also proceeds without any detectable catalysis by the nitric acid formed.[9] However in strongly acidic solutions the existence of a small fraction of the nitrate ester in the form of its conjugate acid is feasible and the extent of conversion into this form would increase with the acidity. The lower stability resulting from loss of resonance stabilisation would be relieved by the loss of a nitronium ion.

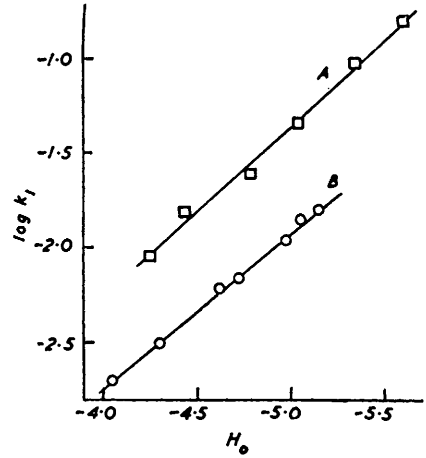

FIG. 1. *A*, $HClO_4$. *B*, H_2SO_4.

Dependence of K_N on the Acidity of the Media.—From the mechanisms which have been deduced for the esterification[1] and the hydrolysis, the equilibrium set up in strongly acidic media between an alcohol and its nitrate ester can be represented by eqn. (7):

$$ROH + NO_2^+ \rightleftharpoons RO\cdot NO_2 + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If K_0 represents the thermodynamic equilibrium constant, then by combining eqns. (7) and (2) we have

$$K_0/K_N = [HNO_3](H^+)f_{RONO_2}/[NO_2^+]f_{ROH}f_{NO_2^+} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where square brackets represent concentrations, parentheses activities, and f activity coefficients. Taking logarithms and combining this with eqn. (9)[5] and (10),[10]

$$H_0 = -\log (H^+)f_B/f_{BH^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$pK_{HNO_3} - pK_{ZOH} = \log ([NO_2^+]/[HNO_3]) - \log ([Z^+]/[ZOH]) \quad . \quad . \quad (10)$$

where B represents a Hammett-type base and ZOH a triphenylmethanol-type compound, we can derive (11):

$$\log K_N - H_0 - \log ([Z^+]/[ZOH]) = \Sigma pK - \Sigma \log f \quad . \quad . \quad . \quad (11)$$

where $\Sigma pK = pK_{HNO_3} - pK_{ZOH} - pK_0$

and $\Sigma \log f = \log (f_{RONO_2}f_{BH^+}/f_{ROH}f_Bf_{NO_2^+})$

If the $\log f$ term is not subject to considerable change over short ranges of media, the left-hand side of eqn. (11) should show some evidence of constancy. For perchloric acid,

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[8] Baker and Neale, *J.*, 1955, 608.
[9] McKinley, McGee, and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247.
[10] Murray and Williams, *J.*, 1950, 3322.

use of log ([Z^+]/[ZOH]) values for the indicator methyl 4-trimethylammoniumtriphenylmethyl ether perchlorate[1] makes the expected constancy quite evident, the sum of the three terms over the range 55—62% perchloric acid being 4·33 ± 0·06. For sulphuric acid, values of C_0 were used in place of the term log ([Z^+]/[ZOH]) since by definition[11] these terms only differ by the constant pK_{ZOH}; when eqn. (11) is tested in this form it is apparent that constancy is attained over the range 62—66% sulphuric acid for isopentyl alcohol and, less definitely, over the range 79—82% sulphuric acid for 2,4-dinitrobenzyl alcohol (see Fig. 2), although these ranges are considerably narrower than in perchloric acid (they correspond to *ca.* 0·5H_0 unit for both sulphuric acid ranges compared with the 1·3H_0 units for perchloric acid).

Previous discussion[1] has indicated that this difference in the two solvents is probably due to a greater diversity in the variation of activity coefficient ratios with composition of the medium in sulphuric acid. It would be useful to extend these studies to other alcohols to see if greater accord between the behaviour of the two solvents is possible in other ranges of media. For this purpose it would suffice to determine the equilibrium composition since eqn. (11) only requires evaluation of K_N and not of individual rate constants; the rapidity with which equilibrium is established is unimportant. In addition, the concurrent sulphation in sulphuric acid does not present any problem provided that analyses can be carried out as in the case of 2,4-dinitrobenzyl alcohol.

In the related equilibria set up when guanidines are nitrated or nitroguanidines denitrated in aqueous strong acids,[12] a direct dependence of the equilibrium constant K on the activity of water present has been found on the assumption that water participates in the equilibrium. The relationship is tested by a plot of log K against log (H_2O) which should give a straight line of negative unit slope. This has not been found to apply to the esterification reported here.

It has been assumed in this discussion that if any protonation of isopentyl alcohol or dinitrobenzyl alcohol occurs in the range of media investigated, this is limited for both compounds to a small amount. The arguments in favour of this view have already been considered for 2,4-dinitrobenzyl alcohol[4] and undoubtedly would apply to isopentyl alcohol. Any extensive change of protonation of either alcohol with increasing acidity in the ranges of media studied would have been revealed in the kinetic analysis.

EXPERIMENTAL

Materials and Media.—The preparation and standardisation of acids and the procedures used for isopentyl alcohol and nitrate have been described.[1] 2,4-Dinitrobenzyl alcohol was prepared[13] from 2,4-dinitrobenzyl chloride by conversion into acetate and hydrolysis of this with 50% sulphuric acid at 120°. The product, crystallised successively from water (with charcoal present), methanol, and benzene, had m. p. 115—116°. 2,4-Dinitrobenzyl nitrate was obtained in excellent yield by the action of freshly prepared anhydrous nitric acid on the alcohol. 15 g. of anhydrous nitric acid were added slowly to 5 g. of 2,4-dinitrobenzyl alcohol with shaking at 0°. After a few minutes, the solution was poured on ice and the yellow oil which separated was allowed to solidify. Recrystallisation gave 4·5 g. (70% yield) of 2,4-dinitrobenzyl nitrate, m. p. 39·5°.

Analysis of Reaction Mixtures.—The residual 2,4-dinitrobenzyl alcohol was determined by oxidation with dichromate in 6N-sulphuric acid by Williams and Clark's[3] method; neither nitric acid nor 2,4-dinitrobenzyl nitrate interfered. In preliminary experiments to find the relative extent of nitration and sulphation, the residual nitric acid was determined by the standard method[14] of reduction with excess of ferrous ammonium sulphate and back-titration

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[11] Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

[12] Simkins and Williams, *J.*, 1952, 3086; Hardy-Klein, *J.*, 1957, 70.

[13] Friedländer and Cohn, *Monatsh.*, 1902, **23**, 546; *Ber.*, 1902, **35**, 1266.

[14] Kolthoff, Sandell, and Mostovitz, *J. Amer. Chem. Soc.*, 1933, **55**, 1454; Lowen and Williams, *J.*, 1950, 3312.

with dichromate; the nitrate ester which would have interfered in this determination was first removed by extraction with carbon tetrachloride. In the experiments in which the presence of excess of nitric acid made this method unsuitable, the carbon tetrachloride extract of nitrate ester was evaporated to dryness and the residual oil dissolved in concentrated sulphuric acid and analysed for nitrate by direct titration with ferrous sulphate solution.[15]

Evaluation of Equilibrium Constants.—For the precise determination of the composition of equilibrium mixtures formed by 2,4-dinitrobenzyl alcohol and nitric acid at 25° a new absorptiometric method was devised for the direct determination of 2,4-dinitrobenzyl nitrate. A 2 ml. sample of the equilibrium mixture was diluted to 6N-sulphuric acid and after oxidation of the unchanged alcohol with dichromate the solution was extracted twice with 10 ml. portions of benzene; this extraction removed both the nitrate ester and the oxidation product, 2,4-dinitrobenzoic acid. The latter was removed by washing the combined benzene extracts twice with 5 ml. portions of 0·2N-sodium hydroxide, and once with water, and then filtering into a 25 ml. flask and making up to the mark with benzene. The absorption of this solution was measured on a Spekker photoelectric absorptiometer having 1 cm. cells with H 556 filters, which give a high transmission of ultraviolet light. The concentration of nitrate ester were obtained from a standard curve previously prepared by using a series of solutions of known concentration in benzene (see Fig. 3). By this method, alcohol and nitrate ester determinations were carried out on the same sample of the equilibrium mixture; · for each experiment, samples were removed at four half-hourly or hourly intervals to confirm that a true equilibrium had been established.

FIG. 2. *A, 2,4-Dinitrobenzyl alcohol; B, Isopentyl alcohol.*

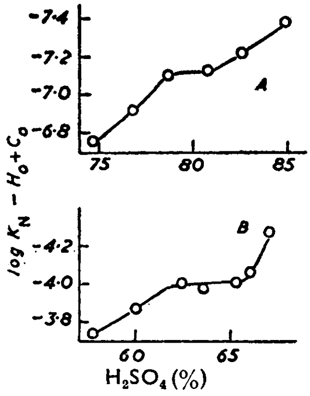
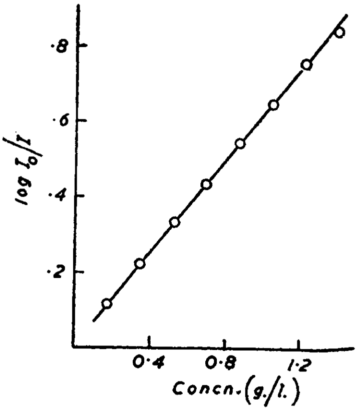


FIG. 3. *2,4-Dinitrobenzyl alcohol.*



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[15] Treadwell and Vontobel, *Helv. Chim. Acta*, 1937, **20**, 573.