786. *Nitration of Alcohols at Oxygen Centres. Part III.*[1] *The Reaction of Nitric Acid and 2,4-Dinitrobenzyl Alcohol in Acetic Anhydride–Acetic Acid Solvent.*

By T. G. Bonner.

The rate of conversion of 2,4-dinitrobenzyl alcohol into its nitrate ester by nitric acid in several acetic anhydride–acetic acid mixtures has been measured. The *O*-nitration proceeds to completion and no acetylation of the alcohol is apparent. The reaction is of the second order with respect to the nitric acid, which suggests that dinitrogen pentoxide formed in fractionally small amount is the active nitrating agent. Within the range of media containing 0—10% of acetic anhydride a maximum rate of reaction appears at about 7% acetic anhydride although at a much higher acetic anhydride content the reaction is immeasurably fast.

The various equilibria which may be present in the system are discussed.

The nitrating property of nitric acid in acetic anhydride first demonstrated by Orton[2] in the nitration of aromatic compounds was until fairly recently assumed to be due to the presence of acetyl nitrate, since preparations of this reagent showed similar nitrating behaviour.[3] A kinetic study[4] of the nitration of benzene by benzoyl nitrate in carbon tetrachloride however has established that in the case of this mixed anhydride a small stationary concentration of the more reactive dinitrogen pentoxide is formed in equilibrium with benzoic anhydride according to eqn. (1), and that the *C*-nitration proceeds solely by attack of the dinitrogen pentoxide and not to any detectable extent directly by benzoyl nitrate. The same report suggests that a similar mechanism is operative in the nitration of benzene by nitric acid and acetic anhydride in carbon tetrachloride[5] and includes the qualitative observation that there is an optimum amount of acetic anhydride, excess of which decreases the rate of nitration by reversing the equilibrium in which the dinitrogen pentoxide is formed.

$$2\mathrm{BzO{\cdot}NO_2} \rightleftharpoons \mathrm{N_2O_5} + \mathrm{Bz_2O} \qquad (1)$$

In the conversion of alcohols into nitrate esters, nitric acid in a mixed solvent of acetic anhydride and acetic acid is frequently used as the nitrating medium.[3,6] The experience gained with 2,4-dinitrobenzyl alcohol in *O*-nitration studies in other media[1] made it possible to investigate whether dinitrogen pentoxide was the essential intermediate in promoting *O*-nitration in acetic anhydride–acetic acid. In this reaction, apart from the problem of the nitrating entity, there is the possibility of a competing acetylation.

Preliminary examination of the interaction of nitric acid with 2,4-dinitrobenzyl alcohol in this system showed that a 90% yield of the nitrate ester was readily attained, and that as a preparative method this procedure was superior to that of using a mixture of nitric acid and sulphuric acid. The method of analysing reaction mixtures of 2,4-dinitrobenzyl alcohol in the latter solvent[1] by quantitative oxidation of the alcohol with acidic dichromate and spectrophotometric determination of the nitrate ester after extraction with benzene was found to be applicable to the acetic anhydride–acetic acid solutions without modification. Some preliminary analyses were carried out in a medium containing about 4% of acetic anhydride in acetic acid to establish whether the amount of nitrate ester formed after different times corresponded to the amount of alcohol consumed. A typical result

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[1] Part II, Bonner and Frizel, preceding paper.

[2] Orton, *J.*, 1902, 806.

[3] Pictet and Khotinsky, *Compt. rend.*, 1907, **144**, 210; *Ber.*, 1907, **40**, 1164.

[4] Gold, Hughes, and Ingold, *J.*, 1950, 2467.

[5] Cohen and Wibaut, *Rec. Trav. chim.*, 1935, **54**, 409.

[6] Boschan, Merrow, and Van Dolah, *Chem. Rev.*, 1955, **55**, 485.

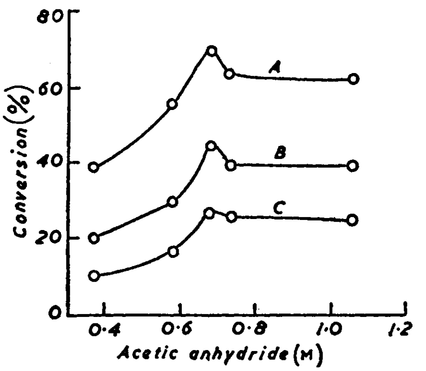
with initial concentrations of *ca.* 0·1M-2,4-dinitrobenzyl alcohol and 0·3M-nitric acid is shown in Table 1. The constancy to within 2% of the sum of the independently determined concentrations of the alcohol and nitrate excludes the possibility that any acetate ester is separately formed in detectable amount concurrently with the nitrate ester. This is in agreement with the failure to detect any acylated product in the nitration of anisole with acyl nitrates in acetonitrile.[7] It is clearly unlikely that the acetate ester has the alternative rôle of a highly reactive intermediate. Experiments to confirm this point showed that over several hours (a period much longer than that required for the completion of the *O*-nitration of the alcohol) added acetate ester was not noticeably attacked by nitric acid in the acetic anhydride–acetic acid solvent, the final analysis showing that at least 96% of the acetate ester remained unchanged.

TABLE 1. *Analysis of an* O-*nitration reaction mixture at 25° in acetic acid containing 0·39*M-*acetic anhydride.*

Initial concns.: [ROH] = 0·1020M; [HNO_3] = 0·3212M.

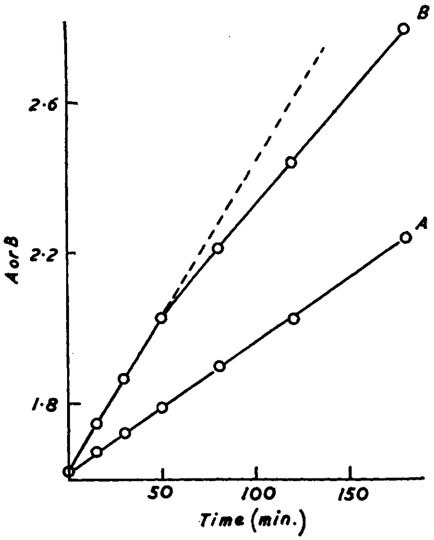
Time (min.)	0	5	10	15	30	60	90	120	150
10^2[ROH] (*A*)	10·20	9·42	8·58	7·87	6·28	4·35	3·05	2·33	1·88
10^2[$RO\cdot NO_2$] (*B*)	0	1·06	1·75	2·48	4·01	6·02	6·99	7·82	8·23
$A + B$	10·20	10·48	10·33	10·35	10·29	10·37	10·04	10·15	10·11

FIG. 1.



A, 100 min.; *B*, 40 min.; *C*, 20 min.

FIG. 2.



$$A = 2{\cdot}3 \log \{(a - 2x)/(b - x)\} + 2x(2b - a)/a(a - 2x).$$
$$B = 2{\cdot}3 \log \{(a - x)(b - x)\} - x(a - b)/a(a - x).$$

Variation of Rate of O-*Nitration with Acetic Anhydride Concentration.*—Measurements of the extent of conversion of 2,4-dinitrobenzyl alcohol into its nitrate ester in a given time showed that the presence of acetic anhydride was essential for reaction, no change being observed when nitric acid alone was present in the acetic acid solvent. Over the range 0—10% (*i.e.*, 0—1M) acetic anhydride there was an increasing rate of conversion into the nitrate ester with increasing acetic anhydride concentration, a maximum rate appearing in the medium containing 7% of acetic anhydride. This is shown in Fig. 1 in which the percentage conversions of 2,4-dinitrobenzyl alcohol into nitrate ester at three separate time intervals for five different acetic anhydride–acetic acid solvents are plotted against

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[7] Burton and Praill, *J.*, 1955, 729.

molarity of acetic anhydride. Although the maximum is clearly evident from the curves, there is only a slight fall in rate from this point to that corresponding to a medium containing 10% of acetic anhydride. Rates of reaction at much higher acetic anhydride concentrations, *e.g.*, 40%, were too fast for measurement so that in the range 10—40% an increase in rate with acetic anhydride content reappears. By means of Fig. 1, the maximum obtained at 7% of acetic anhydride is made evident without knowledge of the mechanism of the reaction. It is also evident that, if the *O*-nitration proceeds exclusively through the action of dinitrogen pentoxide formed by dehydration of the nitric acid and regulated by an equilibrium similar to (1), other equilibria will be necessary to maintain an effective constancy in the fraction of nitric acid converted into dinitrogen pentoxide in media containing acetic anhydride concentrations from 0·7 to 1·06M. An indication of the equilibria set up in these systems has been provided by reports of studies of the physical properties of various mixtures of nitric acid, dinitrogen pentoxide, acetic anhydride, and acetic acid. Vapour-pressure measurements on nitric acid–acetic anhydride mixtures [8] show a maximum near the 1 : 1 mole mixture corresponding to substantially complete formation of acetyl nitrate according to eqn. (2). With increasing nitric acid content

$$Ac_2O + HNO_3 \rightleftharpoons AcO{\cdot}NO_2 + AcOH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

above the 1 : 1 mole mixture, the vapour pressure rises to a maximum at a mole fraction of 0·84 corresponding to formation of dinitrogen pentoxide which can be represented by either equation (3) or (4). Further increase in the nitric acid content decreases the vapour

$$AcO{\cdot}NO_2 + HNO_3 \rightleftharpoons AcOH + N_2O_5 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$Ac_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2AcOH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

pressure until that corresponding to pure nitric acid is finally attained. Raman spectra [9] confirm that, when acetic anhydride is in excess over nitric acid, there is complete conversion of nitric acid into acetyl nitrate and, when nitric acid is in large excess, *i.e.*, >80 moles %, dinitrogen pentoxide is the major product and only traces of acetyl nitrate are present. The formation of acetyl nitrate from nitric acid is represented as the dehydration (4) followed by reaction (5) which is complete when the acetic anhydride is in excess. Mixtures of nitric acid and acetic anhydride in the mole ratio 2 : 1 and of dinitrogen pentoxide and acetic acid with mole ratio 1 : 2 gave the same spectra, confirming the rapid establishment of the equilibrium (4). The ultraviolet spectra of the system dinitrogen pentoxide–acetic anhydride [10] indicated some instability over the range 12—96%; for nitric acid–acetic anhydride mixtures containing more than 96% of nitric acid, the ultraviolet spectra resembled those of high concentrations of dinitrogen pentoxide in nitric acid, while mixtures containing less than 7% of nitric acid had a spectra similar to those of solutions of low concentration of dinitrogen pentoxide in nitric acid. Although these results led Jones and Thorn to suggest that in both cases, *i.e.*, of high and low nitric acid concentrations in acetic anhydride, the operative equilibrium was (4) lying well to the right, their results do not exclude the possibility that acetyl nitrate may be substantially formed at the lower nitric acid concentration. More recently, measurements of the density, viscosity, and refractive index [11] of the systems acetic anhydride–nitric acid and acetic acid–nitric acid have also shown that a 1 : 1 molar mixture of acetic anhydride and nitric acid gives almost complete conversion into acetyl nitrate according to eqn. (2) and that appreciable amounts of dinitrogen pentoxide are only formed according to (4) when the concentration of nitric acid is very high. The conclusion was also reached that acetyl nitrate is not likely to be an intermediate in the formation of dinitrogen pentoxide.

$$N_2O_5 + Ac_2O \rightleftharpoons 2AcO{\cdot}NO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

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[8] Vandoni and Viala, *Mém. services. chim. État*, 1945, **32**, 80.

[9] Chedin and Feneant, *Compt. rend.*, 1949, **229**, 115—117.

[10] Jones and Thorn, *Canad. J. Res.*, 1949, **27***B*, 580—603.

[11] Malkova, *J. Gen. Chem. U.S.S.R.*, 1954, **24**, 1151 (U.S. translation).

The Kinetic Order of the O-Nitration in the Acetic Anhydride–Acetic Acid Solvent.—Before any use could be made of the above data, it was necessary to determine the kinetic order of the *O*-nitration. Some preliminary experiments were carried out with a solvent containing 0·37M-acetic anhydride in acetic acid, using a fixed initial concentration of 0·04M-2,4-dinitrobenzyl alcohol (*b*) for all runs, and systematically increasing the initial nitric acid concentration (*a*) from 0·2 to 0·8M. Higher concentrations of nitric acid appeared to result in some side reactions to give easily oxidisable products which interfered in the method of analysis. The results, although accurately reproducible for duplicate runs, did not satisfy the rate equation for a second-order reaction (*i.e.*, first-order with respect to the alcohol and to the nitric acid), the plots of log $(a - x)/(b - x)$ against time in all cases giving a smooth curve. For reactions in which the nitric acid concentration was in tenfold or greater excess over the alcohol the results were plotted as for a first-order reaction of the alcohol only. Although there was an evident curvature when log $(b - x)$ was plotted against time, rate constants could be calculated from the straight portion of the curve covering up to about 25% conversion of the alcohol into nitrate ester. The significant feature then appeared that the ratio of the rate constant to the square of the initial nitric acid concentration was a constant independent of the latter. The reaction was therefore of the second order with respect to the nitric acid. These results suggested that *O*-nitration did not take place through attack by acetyl nitrate on the alcohol since this would most probably require first-order dependence on the nitric acid. To derive the simplest kinetic equation on the basis of a reaction of the first order with respect to the alcohol and second order with respect to the nitric acid, it was assumed that the two molecules of nitric acid were initially involved in the formation of dinitrogen pentoxide which then reacted with the alcohol.

Stoicheiometrically, in this reaction a molecule of nitric acid is liberated for each molecule of alcohol consumed, and if the reactions are represented as in (6) with the concentrations of the reactants at time *t* as shown, the rate equation can be represented

$$\underset{a-2x}{2\mathrm{HNO_3}} \longrightarrow \mathrm{N_2O_5};\ \underset{b-z}{\mathrm{ROH}} + \mathrm{N_2O_5} \longrightarrow \underset{x}{\mathrm{RO{\cdot}NO_2}} + \underset{x}{\mathrm{HNO_3}} \quad . \;.\; .\; .\; . \quad (6)$$

by eqn. (7) from which the kinetic equation (8) is derived:

$$\mathrm{d}x/\mathrm{d}t = k(a - x)^2(b - x) \quad . \;.\; .\; .\; .\; .\; . \quad (7)$$

$$k(a - b)^2t = 2{\cdot}3 \log \{b(a - x)/a(b - x)\} - (a - b)/a(a - x) \quad . \;.\; . \quad (8)$$

If however the nitric acid liberated in the *O*-nitration is removed, *e.g.*, by conversion into acetyl nitrate as in eqn. (2), the rate equation then becomes that shown in (9) and the derived kinetic equation is (10):

$$\mathrm{d}x/\mathrm{d}t = k(a - 2x)^2(b - x) \quad . \;.\; .\; .\; .\; .\; . \quad (9)$$

$$kt(a - 2b)^2 = 2{\cdot}3 \log \{b(a - 2x)/a(b - x)\} + 2x(2b - a)/a(a - 2x) \quad . \quad (10)$$

With a fixed initial concentration of 2,4-dinitrobenzyl alcohol of 0·04M and with that of the nitric acid within the range 0·2—0·8M, it was found in all cases that the kinetic equation (10) was obeyed. This is demonstrated in Fig. 2 in which the plot of $2{\cdot}3 \log \{(a - 2x)/(b - x)\} + 2x(2b - a)/a(a - 2x)$ against *t* (eqn. 10) is a straight line over the 70% change followed in the reaction while the plot of $2{\cdot}3 \log \{(a - x)/(b - x)\} - x(a - b)/a(a - x)$ (eqn. 8) against *t* deviates markedly from a straight line. With the reactant concentrations indicated, a constant value of *k* is obtained from these plots for kinetic measurements in a given medium, as the results shown in Table 2 for the medium containing 0·37M-acetic anhydride demonstrate. The rate constants obtained from eqn. (10) over the range of media investigated show that there is an optimum acetic anhydride concentration at about 0·7M, as mentioned previously. When the initial concentration of the alcohol is altered, the kinetic equation (10) is still obeyed but the value of the rate constant changes slightly. The effect is small in the 0·37M-medium (experiments 44 and

45) but is more marked in media with a higher acetic anhydride content; a more detailed investigation is necessary to interpret this feature.

Evidently there is more than one reaction scheme which satisfies the kinetic order found experimentally and provides for dinitrogen pentoxide as the active nitrating agent. The main possibilities are shown in (i)—(iv):

TABLE 2. *Rate constants of* O-*nitration of* 2,4-*dinitrobenzyl alcohol in acetic anhydride–acetic acid.* (*Initial concns. shown.*)

Expt.	$[Ac_2O]$ (M)	$10^2[ROH]$ (M)	$10^2[HNO_3]$ (M)	k	Expt.	$[Ac_2O]$ (M)	$10^2[ROH]$ (M)	$10^2[HNO_3]$ (M)	k
41	0·37	4·06	16·37	0·22	29	0·58	4·13	20·45	0·46
43	,,	4·07	16·26	0·20	30	,,	4·09	15·33	0·46
49	,,	4·06	20·48	0·22					
48	,,	4·15	41·80	0·21	26	0·68	4·16	16·20	0·76
50	,,	4·16	40·95	0·21					
51	,,	4·14	63·30	0·22	22	0·73	4·14	21·15	0·67
52	,,	4·16	79·20	0·19	23	,,	4·18	15·86	0·71
44	,,	6·10	21·70	0·18	18	1·06	4·22	15·84	0·65
45	,,	2·13	22·00	0·17	63	,,	4·04	40·20	0·68

(i) $Ac_2O + HNO_3 \rightleftharpoons AcO{\cdot}NO_2 + AcOH$ and either (ii), (iii), or (iv)

(ii) $2AcO{\cdot}NO_2 \rightleftharpoons Ac_2O + N_2O_5$

(iii) $AcO{\cdot}NO_2 + HNO_3 \rightleftharpoons AcOH + N_2O_5$

(iv) $Ac_2O + 2HNO_3 \rightleftharpoons 2AcOH + N_2O_5$

Since the nitration of benzene by pure dinitrogen pentoxide in carbon tetrachloride is immeasurably fast and rate measurements are only possible when deactivating substituents are present,[12] the easier *O*-nitration in acetic anhydride–acetic acid can proceed at a measurable rate only if the fraction of nitric acid present as dinitrogen pentoxide in this system is extremely small. Although reaction (ii) provides an obvious means of interpreting the occurrence of an optimum concentration of dinitrogen pentoxide, it does not account for the immeasurably fast rate at a much higher acetic anhydride concentration. This can be accommodated by reactions (iii) or (iv) since the lower relative amount of acetic acid in such media would correspond to a shift in equilibrium to the right in (iii) and (iv). Further, a large increase in the ratio of acetic anhydride to acetic acid in media containing a very low concentration of perchloric acid ($<0{\cdot}1$M) leads to a considerable increase in the acidity of the medium;[13] this would enhance the formation of dinitrogen pentoxide in both cases.

EXPERIMENTAL

Materials and Media.—2,4-Dinitrobenzyl alcohol and its nitrate ester are described in the preceding paper.[1] " AnalaR " acetic acid was distilled to give a product of m. p. 16·5°. Acetic anhydride, distilled twice through a small fractionating column, was weighed in appropriate amount and made up to a known volume at 25° with the acetic acid; allowance was made for the small amount of water in the acetic acid in calculating the composition of each medium.

Kinetic Measurements.—It was established that the acetic anhydride–acetic acid solvent did not interfere with the methods of determination of 2,4-dinitrobenzyl alcohol (by dichromate oxidation) and of its nitrate ester (spectrophotometrically) previously described.[1] The alcohol was weighed into a B24 cap which fitted the neck of the reaction flask containing 20 ml. of the medium at 25°. The cap was inserted into the neck of the reaction flask at zero time and on vigorous shaking the alcohol dissolved almost instantaneously. The flask was returned to the thermostat at 25° and 2 ml. samples were removed at intervals and run into 10 ml. of a solution of 4 g. of potassium dichromate in 1 l. of 6N-sulphuric acid. Next morning the excess of dichromate was determined with potassium iodide and standard thiosulphate solution by

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[12] Gold, Hughes, Ingold, and Williams, *J.*, 1950, 2452.

[13] MacKenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159.

the usual procedure. When the 2,4-dinitrobenzyl nitrate ester formed was determined simultaneously, the dichromate solutions after the overnight standing were extracted twice with 10 ml. portions of benzene. The extracts were combined, washed with 0·2N-sodium hydroxide, then with water, filtered into 25 ml. volumetric flasks, and made up to the mark with benzene washings.

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