

might be made possible under the influence of the solvent methyl alcohol. The fact that the change is not complete but that an equilibrium exists in methyl alcohol is indicated both (1) by the low value of the magnetic susceptibility and (2) by the effect of dilution on the absorption spectrum, especially in the region governed by the nickel aldimine complex band (step-out) at about 4500 Å.

We might go further and suggest that this equilibrium in methyl alcohol solution consists of approximately one-third of the paramagnetic form and two-thirds of the diamagnetic form of the molecules, since the observed value of the magnetic susceptibility is approximately one-third as great as the value to be expected for a paramagnetic compound of this type.

Confirmation of the interpretation just given for our results comes from further consideration of the curve for residual rotatory dispersion. When the values of $1/M$ are plotted against λ^2 for this curve, the points do not yet lie on a straight line, showing that at least two other absorption bands are optically active. It is possible, but not advisable without further experimental data, to analyze further the residual curve into two others, one governed by the band at 4500, due probably to the nickel aldimine complex, and the second by the far distant band of the camphor radical itself.

Summary

New data are presented on the visible and ultraviolet absorption spectrum of the nickel complex of formylcamphor-ethylenediamine and on its magnetic susceptibility in the solid state and in methyl alcohol solution. From an analysis of the relation between its rotatory dispersion and its absorption spectrum, and from the magnetic susceptibilities, the conclusion is drawn that the configuration of the nickel complex is square coplanar in the solid state, but strained and twisted under the influence of the asymmetric camphor to such an extent that the nickel center in methyl alcohol solution also is asymmetric and tends toward the tetrahedral configuration. New data are also presented for the magnetic susceptibilities of five other organic coordination compounds of nickel: with *o*-hydroxyacetophenone, *o*-hydroxyacetophenone imine, salicylic aldehyde propylenediamine, *o*-amino-benzalimine, and *o*-aminobenzaldehyde phenylenediamine. New data are given for the absorption spectra in the visible and ultraviolet of bis-salicylaldehyde nickel and bis-salicylaldehyde-propylenediamine-nickel. Tentative conclusions are drawn concerning the difference in absorption spectra of paramagnetic and diamagnetic compounds of the types studied.

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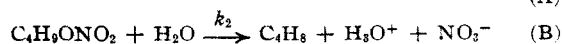
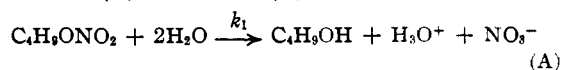
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rate and Mechanism in the Reactions of *t*-Butyl Nitrate and of Benzyl Nitrate with Water and with Hydroxyl Ion¹

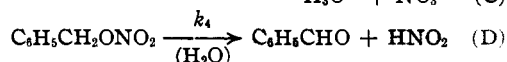
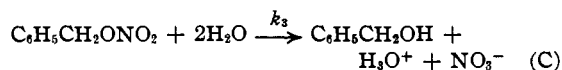
BY GLENNARD R. LUCAS AND LOUIS P. HAMMETT

We have investigated kinetically the reactions with water and hydroxyl ion of two alkyl nitrates which illustrate the two kinds of reactions other than hydrolysis which such substances undergo in the presence of water.²

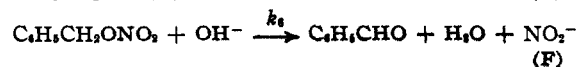
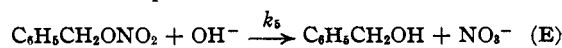
In the case of tertiary butyl nitrate the only reactions are the two solvolytic ones producing alcohol (A) and olefin (B).



In the case of benzyl nitrate no olefin is produced but the solvolysis to benzyl alcohol and nitric acid (C) is accompanied by a likewise first order formation of benzaldehyde and nitrous acid (D).



These first order reactions are accompanied by second order reactions with hydroxyl ion leading to the same products.



(1) Dissertation submitted by Glennard Ralph Lucas in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) Klason and Carlson, *Ber.*, **59**, 2752 (1906); **40**, 4183 (1907); Carlson, *ibid.*, **40**, 4191 (1907).

Experimental

Apparatus.—Only calibrated weights and volumetric apparatus were used. The temperatures were determined by thermometers calibrated by the Bureau of Standards. The thermostats used at 25 and 50° were of the conventional type; that employed at 0.3 and 10° was the one previously described.³ The timing of the very fast runs was done with an A. R. & J. E. Meylan one-fifth second split timer.

Tertiary Butyl Nitrate.—Following the procedure of Michael and Carlson,⁴ *t*-butyl nitrate was prepared from tertiary butyl alcohol (Eastman Kodak Co. best grade) and 98.6% nitric acid. The product was separated by distillation under vacuum through a 20-in. jacketed column with reflux ratio kept high by means of a cold-tip finger condenser; b. p. 22–23° at 4 mm. The last traces of methylene chloride and nitric acid were removed by repeated partial crystallization without solvent. The crystals were allowed to form slowly until approximately three-fourths was crystallized and the remaining liquid removed through a sintered glass filter. The degree of purity was tested in an air-jacketed test-tube cooled by solid carbon dioxide at a rate of one degree per minute. The material accepted as pure gave a constant freezing point out to half crystallization, was colorless and free from acid; m. p. –34 to –35°. Titration of the acid formed on complete hydrolysis indicated 99.9% purity. For further test 5.00 g. of the *t*-butyl nitrate was added to 8.0 g. of dimethylaniline and warmed. The nitrate salt which crystallized on cooling was washed free of dimethylaniline with dry ether, yielding 7.21 g.; calcd. 7.23; m. p. 82–83°.

In some preparations, the ester was colorless but not free from acid after the above recrystallization procedure. Rate measurements on this ester agree within experimental error with those made on the pure material when allowance is made for the effect of electrolyte. The purified ester was sealed in amber ampoules and kept frozen in dry-ice until used.

Benzyl Nitrate.—Following the procedure of Nef,⁵ benzyl nitrate was prepared from powdered silver nitrate and benzyl chloride (Mallinckrodt Analytical grade) in dry ether. For complete conversion it was found desirable to add fresh silver nitrate from time to time. After twenty hours at room temperature the ether was distilled off and the product held at 70–75° for five hours. After cooling, the liquid was decanted and the residue extracted with ether and dried over calcium chloride. Fresh silver nitrate was added to the filtered ether solution, the ether removed and the benzyl nitrate distilled directly from silver nitrate. The main fraction (b. p. 72.5–73.5° at 4–5 mm.) was found by refluxing with alcoholic silver nitrate to be chloride free, n_D^{25} 1.5180. Redistillation gave fractions with the same constant refractive index. *Anal.* Calcd. for C₇H₇NO₂: C, 54.9; H, 4.61. Found: C, 55.2; H, 4.63. The purified ester was kept in a dark bottle in a desiccator over phosphorus pentoxide.

Other Materials.—1,4-Dioxane (Carbide and Carbon Chemical Co.) was purified in 3–4 liter quantities as described by Beste and Hammett.⁶

Sodium perchlorate solution was prepared from Mallinckrodt A. C. S. grade perchloric acid 99.8% neutralized with carbon dioxide-free sodium hydroxide solution. Tests on this solution showed no detectable traces of chloride. The perchloric acid solution that was added to runs was made from the same stock acid.

The potassium bromide and potassium bromate used for the olefin determination and the potassium nitrate and lithium nitrate used in the runs were A. C. S. grade, recrystallized from water and dried over phosphorus pentoxide. Anhydrous lithium nitrate is so hygroscopic that the concentration was probably lower than that indicated because of water absorbed in the weighing process.

The primary standard for titration was Bureau of Standards acid potassium phthalate.

Method.—The solvent in all kinetic experiments was a mixture of dioxane and water in the proportions indicated; that is, in an experiment in "60% dioxane" the proportions of dioxane and water were 60 to 40 by weight. In the case of experiments containing sodium hydroxide, sodium perchlorate or perchloric acid, these solutes were introduced as solutions at the time the solvent was prepared, and correction was made for the amount of water displaced by these solutes. All other solutes were weighed out and added directly.

In starting experiments the reaction bottle with all solutes except the ester was placed in the thermostat to reach temperature equilibrium. In the case of *t*-butyl nitrate, the ester was then removed from the dewar where it was stored, allowed to melt and the approximate amount transferred by means of a graduated pipet, the bottle was shaken and the initial time taken. The exact initial ester concentration was determined by delivering duplicate samples into 40% dioxane at room temperature. The hydrolysis in this medium is complete in a few minutes and the total ester concentration was found by titration of the acid produced. Samples for analysis were withdrawn at convenient intervals using a 5-ml. pipet and delivered into cold dioxane of such volume that in the following titration the dioxane composition always exceeded 80%. In the runs at 0 and 10° the pipet was kept in a well in the thermostat between samples.

In the case of benzyl nitrate, after the mixture had reached temperature equilibrium in the thermostat, the ester was weighed in and the initial time taken. At convenient intervals 10-ml. samples were withdrawn for analysis. In the runs at 50° the dried pipet, initially at room temperature, delivered reproducible volumes of the reaction solution if the sampling was done rapidly. The water reaction was arrested by pipetting the samples into dioxane at room temperature. The hydroxide reaction was stopped by pipetting the samples into an excess of standard nitric acid and dioxane. To reduce further reaction to a negligible level and to prevent the unreacted benzyl nitrate from separating, the dioxane was kept above 50% in the titrating flask. In the solvolytic runs where the percentage benzaldehyde was determined the solvent containing all solutes except the ester was cooled to ice temperature, the ester added and portions of this reaction mixture were placed in 10-ml. ampoules. After freezing solid in a dry-ice bath the ampoules were evacuated and sealed. The initial time was taken when the ampoules were placed in the thermostat.

(3) Price and Hammett, *THIS JOURNAL*, **63**, 2389 (1941).

(4) Michael and Carlson, *ibid.*, **57**, 1268 (1935).

(5) Nef, *Ann.*, **309**, 171 (1899).

(6) Beste and Hammett, *THIS JOURNAL*, **63**, 2481 (1940).

Isobutene was determined by a modification of the method of Lucas and Eberz⁷ using a standard bromide-bromate solution to liberate bromine and back-titrating with thiosulfate after conversion to iodine. The sample was delivered into glass-stoppered iodine flasks containing a five-fold excess of the neutral bromide-bromate solution; 5 ml. of 6 *N* sulfuric acid was quickly added and the walls washed down with 15 ml. of water. After tightly stoppering, the flask was kept in the dark and shaken frequently for five minutes. The flask was then chilled under running water and saturated, freshly-prepared potassium iodide solution was allowed to be sucked in by carefully lifting the stopper slightly. When a few cc. had been admitted, the stopper was replaced and the flask thoroughly shaken. The stopper was washed free of iodine and removed, and the excess iodine was titrated with thiosulfate. The blank depends slightly on the volume of dioxane in the sample and is reproducible. A correction must be made for the olefin produced by the nearly instantaneous hydrolysis of the unreacted *t*-butyl nitrate. Using the above procedure with *t*-butyl nitrate in 100% dioxane, four blank experiments showed that 2.99 ± 0.01% of the ester was converted to isobutene during its rapid hydrolysis.

Benzaldehyde was determined by the method of Eitel and Lock,⁸ by producing the 2,4-dinitrophenylhydrazone of benzaldehyde and determining it gravimetrically. For small samples drying to constant weight in a vacuum desiccator over phosphorus pentoxide was found more satisfactory than heating in the oven. To prevent the separation of unreacted benzyl nitrate the samples of solution tested had to be kept small. Somewhat larger samples could be added where the precipitating medium for the hydrazone was 50% cold alcohol. The two methods gave consistent results when used in the runs or with standard solutions of benzaldehyde to which benzyl nitrate had been added.

In following the acid production, phenolphthalein is unsatisfactory where much dioxane is present. Brom cresol purple gave a sharp end-point in media containing about 50% dioxane and was consequently used in titrations of the benzyl nitrate runs. Brom phenol blue gave a very sharp end-point in 80–90% dioxane and was used in the *t*-butyl nitrate runs.

Rate Calculations.—The following abbreviations will be used in this section: *a* is the initial concentration of tertiary butyl nitrate, *b* initial concentration of hydroxide, *c* initial concentration of benzyl nitrate, *x* concentration of acid produced at time *t*, *t* time in seconds. The *t*-butyl group will be written Bu, the benzyl group Bz and the phenyl group Ph.

Data for the water reactions (A) and (B) were calculated according to the equation $\ln a/(a - x) = kt$ where $k = k_1 + k_2$; $a = [H^+]_\infty$ or $\{[H]^+_\infty - [H^+]_0\}$ in the cases where $[H^+]_0 \neq 0$ and $(a - x) = [H^+]_\infty - [H^+]_t$. The slope of the plot of $\ln(a - x)$ against *t* increases slightly

during the course of a given experiment. For purposes of comparison the initial value of *k* was obtained from the empirical equation $-\ln(a - x) = -\ln a + (k)_0 t + Kt^2$; the coefficients of this equation were calculated by the method of averages,⁹ whereby adjacent experimental points were used to obtain each of the three simultaneous equations. The values of k_1 and k_2 were established by determination of the per cent. olefin produced.

In the runs in the presence of sodium chloride and sodium toluenesulfonate the curve follows too complicated a course to be satisfied by this three constant equation. This is probably because the nitrate ester is gradually being replaced by chloride or toluenesulfonate ester which have slower rates of hydrolysis. Here the initial rates were determined by means of graphical differentiation.

Data for the water reactions of benzyl nitrate (C) and (D) were calculated according to the equation $\ln c/(c - x) = k't$ where $k' = k_3 + k_4$. Here again the plot of $\ln(c - x)$ against time gave an increasing slope and the initial value was found by the method of averages. The respective values of k_3 and k_4 were established by determination of the per cent. benzaldehyde produced.

In the presence of hydroxyl ion we are concerned with reactions (C), (D), (E) and (F). The rate of disappearance of nitrate ester is given by

$$-d[BzNO_3]/dt = k_3[BzNO_3] + k_4[BzNO_3] + k_5[BzNO_3][OH^-] + k_6[BzNO_3][OH^-] \quad (1)$$

which may be written

$$-d[BzNO_3]/dt = k'[BzNO_3] + k''[BzNO_3][OH^-] \quad (2)$$

where

$$k' = k_3 + k_4 \text{ and} \quad (3)$$

$$k'' = k_5 + k_6 \quad (4)$$

The above equation is best solved by writing in the form

$$-d[BzNO_3]/dt = k'''[BzNO_3][OH^-] \quad (5)$$

where

$$k''' = k'' + (k'/[OH^-]) \quad (6)$$

The value of k''' may be obtained by a plot of $\frac{1}{c-b} \ln \frac{c-x}{b-x}$ against time. The method of averages is again used to determine the initial value of the slope. The value of $(k'')_0$ may then be evaluated from equation (6) using the $(k')_0$ independently determined from hydrolysis measurements. Some uncertainty exists concerning the value of $(k')_0$ to be used. Those independently

(7) Lucas and Eberz, *ibid.*, **56**, 461 (1934).

(8) Eitel and Lock, *Monatsh.*, **72**, 385 (1939).

(9) Daniels, "Mathematical Preparation for Physical Chemistry," McGraw Hill Book Co., Inc., New York, N. Y., 1928, p. 235.

measured were of necessity obtained in the absence of hydroxyl ion. The data on *t*-butyl nitrate indicated that a solvolysis reaction may proceed more slowly in the presence of hydroxyl ion than in the solvent alone and at a much slower rate than in the presence of a corresponding concentration of sodium perchlorate. The rate constants were therefore evaluated on the assumption that $(k')_0$ is not changed by the addition of sodium hydroxide.

Examination of these four equations shows that the rate of benzaldehyde production is given by

$$d[\text{PhCHO}]/dt = k_1[\text{BzNO}_2] + k_2[\text{BzNO}_2][\text{OH}^-] \quad (7)$$

and combining equations (5) and (7), we obtain

$$\text{Fraction PhCHO formed in reaction} = \frac{k_1[\text{BzNO}_2] + k_2[\text{BzNO}_2][\text{OH}^-]}{k''[\text{BzNO}_2][\text{OH}^-]} \quad (8)$$

Solving for k_2

$$k_2 = k''x (\text{fraction PhCHO}) - (k_1/[\text{OH}^-]) \quad (9)$$

and using this value of k_2 we obtain k_3

$$k_3 = k'' - k_2 \quad (10)$$

Errors.—Since the results of this research are based on the determination of initial slopes of curves, it is difficult to estimate the precision with which specific rates are known. In general it involves a consideration of duplicate experiments and of the deviation of the individual points of the run from the empirical equation which best fits the data. Careful examination of the data indicates a probable error of 1.5% in $(k)_0$ and $(k')_0$ each of which is the sum of two solvolytic reactions. The percentage of olefin produced is the average of two or three independent determinations and the precision varies from 1 part in 50 to 1 part in 400 as the proportion of olefin increases. Consequently the precision of the constant k_2 varies in the same way. The error in k_1 will be about the same as that in k . The reported percentage of benzaldehyde is also the average of two or more determinations and the precision varies from 1 part in 5 to 1 part in 60 according to the proportion of benzaldehyde. The initial specific rate constants $(k''')_0$ in the hydroxide reaction have a probable error of 2.0 to 2.5% but the lack of precision in the benzaldehyde determination increases the probable error of $(k_2)_0$ and $(k_3)_0$ to 3–5%.

Sample Data.—For the sake of uniformity the constants reported in the tables of results are those at the initial time. It is, however, of some im-

portance to indicate how the specific rate changes during the course of a reaction; a skeleton record is therefore given for a typical experiment on each of the reactions studied (Tables I, II and III).

In Table I the values of k were calculated from the empirical equation

$$-\ln(a-x) = 2.3497 + (3.335 \times 10^{-6})t + (8.92 \times 10^{-11})t^2$$

This equation was obtained from the experimental points of Table I by grouping the first three, the second three and the last three to obtain three simultaneous equations according to the method of averages mentioned above. For the olefin determination the ester concentration was found by solving the above equation for $(a-x)$ at the given time. Applying the correction for the olefin produced by the unreacted butyl nitrate, the percentage of x , or moles reacted, going to olefin is determined. The isobutene concentration given in quotation marks is the indicated olefin concentration from the thiosulfate titer, before the correction is made.

TABLE I

TYPICAL EXPERIMENTAL RECORD FOR THE WATER REACTION OF *t*-BUTYL NITRATE, TIME IN SECONDS
Expt. 63: 85% dioxane at 25°; initial concn. $\text{BuNO}_2 = 0.09543$

<i>t</i> , sec.	Acid titer ^a	$[\text{H}_2\text{O}^+]$	$-\ln[\text{BuNO}_2]$	$(k) \times 10^4$
0		0.00490	2.3497	3.335
300	1.11	.00589	2.3601	3.340
4080	3.24	.01719	2.4876	3.407
5640	4.04	.02144	2.5400	3.435
7680	5.05	.02680	2.6104	3.472
10140	6.20	.03290	2.6970	3.515
11580	6.84	.03629	2.7487	3.542
16920	8.96	.04754	2.9419	3.637
19860	10.00	.05306	3.0523	3.688
25260	11.59	.06123	3.2420	3.785

<i>t</i> , sec.	x	Thio-sulfate titer ^b	" $[\text{C}_4\text{H}_8]$ "	$[\text{C}_4\text{H}_8]$	% Olefin
26400	0.05828	2.38	0.01012	0.00901	15.46
28260	.06080	2.39	.01017	.00913	15.02
623000	.09543	3.49	.01484	.01484	15.53
				Av.	15.35

^a In ml. of 0.02652 *N* NaOH per 4.998 ml. sample.

^b In ml. of 0.04251 *M* $\text{Na}_2\text{S}_2\text{O}_3$ per 4.998 ml. sample.

In Table II the values of (k') were calculated from the empirical equation

$$-\ln(c-x) = 2.2562 + (1.571 \times 10^{-6})t + (2.16 \times 10^{-13})t^2$$

This equation was obtained like the one for Table I by grouping the points in threes to make three simultaneous equations. The amount of benzal-

dehyde was determined gravimetrically in the way indicated and converted to molar concentration of aldehyde.

TABLE II

TYPICAL EXPERIMENTAL RECORD FOR THE WATER REACTION OF BENZYL NITRATE, TIME IN SECONDS
Expt. 151: 60% dioxane at 50°; initial concn. BzNO₂ = 0.10530.

<i>t</i> , sec.	Acid titer ^a	[H ₃ O ⁺]	- ln[BzNO ₂]	(<i>k</i> ') × 10 ⁴
0	0	0	2.2562	1.571
10872	0.86	0.00227	2.2731	1.576
52524	3.36	.00887	2.3393	1.594
77436	4.79	.01264	2.3793	1.604
104184	6.28	.01658	2.4226	1.616
143712	8.35	.02204	2.4862	1.633
169200	9.64	.02545	2.5280	1.644
229608	12.50	.03300	2.6273	1.670
256320	13.75	.03629	2.6740	1.682

<i>t</i> , sec.	<i>x</i>	2,4-Dinitro-phenyl-hydrazone, ^b g.	[PhCHO]	% PhCHO
400068	0.05131	0.0098	0.003351	6.5
582912	.06633	.0116	.003966	6.0
			Av.	6.25

^a In ml. of 0.02652 *N* NaOH per 10.047 ml. sample.

^b From 10.222 ml. sample.

In Table III the values of (*k*'') were calculated from the empirical equation

$$\frac{1}{b-c} \ln \frac{b-x}{c-x} = 10.959 + (4.69_3 \times 10^{-4})t + (3.97 \times 10^{-9})t^2$$

This equation was obtained from the experimental points by grouping as before. The value of *x* was obtained from this equation for the calculation of the per cent. benzaldehyde produced. While in this

experiment the percentage converted to benzaldehyde appears to increase slightly during the course of the reaction, this effect was not reproducible and in calculation of (*k*₃) and (*k*₆) by equations (9) and (10) the average value was used.

Results

Data for tertiary butyl nitrate solvolysis in the presence and in the absence of various salts are given in Tables IV and V, the data being subdivided according to the medium and temperature indicated. In the experiments listed in Table IV only the total rate constant (*k*)₀ was determined, while in those in Table V (*k*)₀ is divided into (*k*₁)₀ and (*k*₂)₀ and the percentage olefin produced is indicated. By comparison of Table I and Table IV it may be seen that the values of *k* in a given reaction mixture drift upward as the reaction proceeds approximately as one would predict from the changing ester concentration and the increasing concentration of nitrate ion.

Data for benzyl nitrate solvolysis in 60% dioxane at two temperatures are given in Table VI, the constants listed being (*k*')₀ the sum in each case of (*k*₃)₀ and (*k*₄)₀; in Table VII experiments where the percentage benzaldehyde produced was determined are listed and the corresponding values of (*k*₃)₀ and (*k*₄)₀ are indicated. In Table VIII are listed data showing (*k*₅)₀ and (*k*₆)₀ for the benzyl nitrate-hydroxyl ion reaction.

In Table IX are listed the energies of activation of the various reactions.

TABLE III

TYPICAL EXPERIMENTAL RECORD FOR HYDROXYL ION REACTION OF BENZYL NITRATE, TIME IN SECONDS

Expt. 138: 60% dioxane 50°; initial concn. BzNO₂ = 0.07499; NaOH = 0.10961

<i>t</i> , sec.	[OH ⁻]	[BzNO ₂]	<i>k</i> ' × 10 ⁴	<i>k</i> ' × 10 ⁴	<i>k</i> ₃ × 10 ⁴	<i>k</i> ₄ × 10 ⁴
0	0.10961	0.07499	4.693	4.546	1.594	2.952
804	.10709	.07247	4.757	4.606	1.616	2.990
2208	.10194	.06732	4.878	4.719	1.656	3.063
3450	.09727	.06265	4.967	4.799	1.687	3.112
4692	.09373	.05911	5.066	4.891	1.720	3.171
7530	.08674	.05212	5.291	5.101	1.796	3.305
9876	.08175	.04713	5.477	5.274	1.853	3.416
11790	.07768	.04306	5.629	5.415	1.909	3.506
15078	.07248	.03786	5.890	5.659	1.997	3.662
17712	.06770	.03308	6.09	5.851	2.067	3.784

<i>t</i> , sec.	<i>x</i>	2,4-Dinitrophenylhydrazone, ^a g.	[PhCHO]	% PhCHO
7608	0.02306	0.0223	0.00776	33.7
17604	.04260	.0426	.01482	34.8
			Av.	34.2

^a From 10.047 ml. sample.

TABLE IV

INITIAL SPECIFIC RATES OF SOLVOLYSIS OF TERTIARY BUTYL NITRATE, TIME IN SECONDS

<i>t</i> , °C.	% Dioxane in solvent	Initial concn. BuNO ₂	Added solutes concn. mole/l.	(<i>k</i>) ₀ × 10 ⁴
25	95	0.12784	HNO ₃	0.0230
25	95	.11711	HNO ₃	.0185
25	85	.12527	HNO ₃	.0159
25	85	.12410	HNO ₃	.0190
25	75	.13282	HNO ₃	.0136
25	75	.12966	HNO ₃	.0168
25	75	.10751	NaClO ₄	.1109
25	75	.10688	LiNO ₃	.1062
25	75	.10673	KNO ₃	.1060
25	75	.10530	NaTs	.1053
25	75	.10390	NaClO ₄	.1111
25	75	.10351	None	2.017
25	75	.10331	KNO ₃	.1060
25	75	.10246	NaCl	.1065
25	75	.10172	HClO ₄	.1158
25	75	.10083	NaCl	.1064
25	75	.09834	NaClO ₄	.0840
			NaOH	.0280
25	75	.09047	None	2.002
25	60	.14325	HNO ₃	.0112
25	60	.13922	HNO ₃	.0080
25	60	.05111	None	16.53
10	60	.07251	NaOH	.1096
10	60	.06975	NaClO ₄	.1128
10	60	.06540	None	2.375
0.3	75	.14937	HNO ₃	.0174
0.3	60	.14263	HNO ₃	.0129
0.3	60	.13952	HNO ₃	.0129
0.3	60	.06918	None	.5580
0.3	60	.06818	NaClO ₄	.1133

thoroughly studied reactions of tertiary butyl halides, which likewise lead partly to alcohol and partly to olefin.¹¹

Like benzyl chloride in a similar medium⁶ benzyl nitrate shows a solvolytic reaction which predominates in neutral or acid media and a hydroxyl ion displacement which predominates in alkaline media. These reactions are accompanied by an oxidation-reduction reaction producing benzaldehyde which is both solvolytic and hydroxyl ion catalyzed.

Our data show that none of these reactions are catalyzed by acids in dilute solution.

Salt and Medium Effects.—As has been observed previously with other esters,^{6,12} the specific rates of the solvolytic reactions (A) and (C) decrease with increasing concentration of ester. Table IV shows the sensitivity of such reactions to the composition of the medium, the rate increasing somewhat more than a thousand-fold in going from 95% to 60% dioxane, the temperature remaining constant. Table X shows for a 0.1 *M* solution of ester the percentage changes in specific rate produced by the addition of various solutes in the same concentration.

Similar but even larger effects are observed in the second order displacement reaction of benzyl nitrate with hydroxyl ion. At 25° (*k*₂)₀ is essentially unaffected by variations in concentration of ester and of hydroxyl ion. However, at 50°

TABLE V

INITIAL SPECIFIC RATES OF SOLVOLYSIS OF TERTIARY BUTYL NITRATE, (*k*)₀, (*k*₁)₀, AND (*k*₂)₀, TIME IN SECONDS

<i>t</i> , °C.	% Dioxane in solvent	Initial concn. BuNO ₂	Added solutes concn., mole/l.	(<i>k</i>) ₀ × 10 ⁴	% Olefin	(<i>k</i> ₁) ₀ × 10 ⁵	(<i>k</i> ₂) ₀ × 10 ⁵
25	95	0.11402		0.1429	44.91	0.0787	0.0642
25	85	.09543		3.335	15.35	2.821	.512
25	75	.15898		19.27	8.71	17.59	1.68
10	60	.12697	NaOH	0.1069	21.16	5.35	20.03
10	60	.12454			21.86	4.76	20.82
10	60	.12389	NaClO ₄	.1124	25.77	4.50	24.61
0.3	60	.12992			5.167	4.24	4.948
0.3	60	.12598	NaClO ₄	.1127	6.168	4.05	5.918

Discussion

General.—Like other *t*-butyl esters¹⁰ the nitrate ester shows no acceleration of hydrolysis by hydroxyl ion except at high concentration of dioxane (see Table IV, hydroxide-perchlorate solute in 75% dioxane). In 60% dioxane a small retardation is produced by sodium hydroxide, the occasion for which will be discussed later. In all important respects the reaction behaves like the

(*k*₂)₀ increases with decreasing concentration of either reactant, increasing by 57.0% in going from the largest ester and hydroxyl ion concentration to the lowest in each. At both temperatures (*k*₂)₀ shows an increase with decreasing ester concentration and a decrease with decreasing hydroxyl ion concentration. Since the ionic strength is maintained constant by the introduction of sodium perchlorate, the change in rate

(10) (a) Hughes, *J. Chem. Soc.*, 225 (1935); Cooper and Hughes, *ibid.*, 1183 (1937).

(11) Bateman, Cooper, Hughes and Ingold, *ibid.*, 925 (1940).

(12) McCleary and Hammett, *THIS JOURNAL*, 63, 2254 (1941).

TABLE VI
INITIAL SPECIFIC RATES OF SOLVOLYSIS OF BENZYL
NITRATE IN 60% DIOXANE, TIME IN SECONDS

Initial concn. BzNO ₃	Added solutes concn., mole/l.	(k') ₀ × 10 ⁶
At 50°		
0.14971		1.484
.14913	KNO ₃ 0.1084	1.516
.14833	NaClO ₄ .1083	1.672
.12078	NaClO ₄ .1088	1.732
.10043	KNO ₃ .1063	1.627
.09639		1.573
.09507		1.595
.09085	KNO ₃ .1090	1.591
.09068	NaClO ₄ .1091	1.869
.09050		1.579
.09038	HClO ₄ .1103	1.835
.09038	NaClO ₄ .1080	1.868
.06063	NaClO ₄ .1096	1.884
At 25°		
.15239		.06675
.13703	NaClO ₄ .1108	.07861
.11079	NaClO ₄ .1110	.07867
.09116		.07072
.06115	NaClO ₄ .1119	.08503

Energies of Activation.—The Arrhenius energies of activation appear in Table IX. Those for *t*-butyl nitrate are in excellent agreement with those observed in the unimolecular reactions of alkyl halides^{10b} which all lie within the range 22 ± 2 kcal. The difference between *k*₁ and *k*₂ is consistent with those observed for unimolecular solvolytic reactions of secondary and tertiary halides and for alkyl sulfonium ions where the increases in the proportion of olefin produced with rise of temperature correspond to activation energies which are larger by about 2–5 kcal. for the elimination than for the substitution.¹³

The energy of activation for the solvolytic reaction (*k*₃)₀ of benzyl nitrate is appreciably larger than that for benzyl chloride,¹⁴ being 24,170 as compared to 20,600. The energy of activation for the hydroxyl ion displacement (*k*₅)₀ is even more strikingly higher than for the corresponding displacement reactions of benzyl chloride; 23,970 compared with 18,400 for the hydroxyl ion dis-

TABLE VII
INITIAL SPECIFIC RATES OF SOLVOLYSIS OF BENZYL NITRATE (*k'*)₀, (*k*₂)₀ AND (*k*₃)₀ IN 60% DIOXANE, TIME IN SECONDS

Initial concn. BzNO ₃	Added solutes concn., mole/l.	(k') ₀ × 10 ⁷	% PhCHO	(k ₂) ₀ × 10 ⁷	(k ₃) ₀ × 10 ⁷
At 25°					
0.15109	NaClO ₄ 0.1106	0.7289	7.2	0.6764	0.0525
.13001		.6478	8.6	.5921	.0557
.10402	NaClO ₄ .1113	.7697	8.8	.7020	.0677
At 50°					
.10530		15.71	6.25	14.73	.98
.07843	NaClO ₄ .1094	18.55	7.4	17.18	1.37
.07996	H ₂ O	16.65	None		
.07524	(Solv. aged 2½ weeks)	15.80	13.5	13.67	2.13
.07115		16.48	7.2	15.29	1.19

TABLE VIII
INITIAL SPECIFIC RATES OF THE HYDROXYL ION REACTION (*k''*)₀, (*k*₅)₀ AND (*k*₆)₀ OF BENZYL NITRATE IN 60% DIOXANE
TIME IN SECONDS

Initial concn. BzNO ₃	Initial concn. NaOH	Concn. NaClO ₄	(k'') ₀ × 10 ⁴	(k') ₀ × 10 ⁴	% PhCHO	(k ₅) ₀ × 10 ⁴	(k ₆) ₀ × 10 ⁴
At 50°							
0.16321	0.05374	0.05409	3.675	3.403	42.5	1.855	1.548
.15721	.10836		3.755	3.620	33.6	2.365	1.255
.07962	.05435	.05470	5.093	4.798	39.0	2.834	1.964
.07499	.10961		4.693	4.546	34.2	2.952	1.594
At 25°							
.14802	.05505	.05540	0.2983	0.2870	67.8	0.0858	0.2012
.14776	.11096		.3133	.3077	67.5	.0967	.2110
.07850	.05556	.05592	.3064	.2935	65.0	.0955	.1980
.07835	.11202		.3389	.3325	58.0	.1365	.1960
.07880	.11161	(aged) ^a	.4144	.4080	53.6	.1865	.2215
.07764	.11104	H ₂ O = .0500	.5769	.5704	None		

^a Solvent aged 2½ weeks at 50°.

with hydroxyl ion must be due to the effect of replacing perchlorate ions by hydroxyl ions in the reaction medium.

(13) For a comprehensive review and references, see Hughes and Ingold, *Trans. Faraday Soc.*, 657 (1941).

(14) (a) Weber, *Rec. trav. chim.*, 53, 869 (1934); (b) Bennet and Jones, *J. Chem. Soc.*, 1815 (1935).

TABLE IX
ENERGIES OF ACTIVATION FOR THE VARIOUS REACTIONS
[ESTER] = 0.100

Spec. rate constant	Medium	Temp. range	$E_{act.}$, cal.
k	75% Dioxane	0.3-25	22,800
k	60% Dioxane	0.3-10	22,870
k	60% Dioxane	10 -25	(22,010) ^c
k_1	60% Dioxane	0.3-10	22,810
k_2	60% Dioxane	0.3-10	24,730
k_3	60% Dioxane	25 -50	24,170
k_4	60% Dioxane	25 -50	21,570
k_5	60% Dioxane	25 -50	23,970
k_6	60% Dioxane	25 -50	14,920

^c Less reliable because it involves the constant at 25° where the error is probably rather high.

TABLE X
PERCENTAGE CHANGE IN SPECIFIC SOLVOLYSIS RATE OF
0.1 M ESTER CAUSED BY ADDITION OF INDICATED SOLUTES
AT 0.108 M CONCENTRATION

t , °C.	% Dioxane in solvent	Solute	% Change in spec. rate
For BuNO ₂			
0.3	60	NaClO ₄	+19.24
10	60	NaClO ₄	+16.48
10	60	NaOH	- 4.28
25	75	NaClO ₄	+37.21
25	75	HClO ₄	+36.62
25	75	KNO ₃	+16.12
25	75	NaCl	+10.30
25	75	C ₇ H ₇ SO ₃ Na	+10.30
For BzNO ₂			
25	60	NaClO ₄	+16.38
50	60	NaClO ₄	+15.62
50	60	HClO ₄	+15.51
50	60	KNO ₃	+ 2.67

placement of benzyl chloride in 50% acetone^{14a} and with 18,300 for the iodide ion displacement of benzyl chloride in acetone.^{14b} The significance of these differences will be discussed under the mechanism of the solvolytic reaction.

Kinetics of the Elimination Reaction.—Table V gives the proportions of olefin formed in the solvolysis of tertiary butyl nitrate in various media at various temperatures. These correspond in every way with those observed for tertiary butyl halides in water-alcohol media.¹³ In agreement with the *t*-butyl halides the ratio of elimination to the over-all reaction decreases as the ionizing power of the medium increases and increases with increasing temperature. The rate constant (k_2)₀ is unchanged by the basicity of the reagent (comparison of hydroxyl ion and perchlorate ion runs) and has a positive salt effect. The latter feature has not heretofore been reported for such reactions and is probably, although

not certainly, beyond experimental error. As indicated in Table IX the increase in per cent. olefin with rising temperature leads to a difference in the energies of activation of the two competing solvolytic reactions of approximately two kilo-calories.

Mechanism of the Solvolytic Reaction.—The reaction of an alkyl nitrate with water may be (1) a displacement of nitrate ion by a water molecule; (2) a true solvolysis, *i. e.*, an incipient solvation of the anion leading to a rupture of the carbon-oxygen bond with more or less transient formation of a carbonium ion; (3) a rupture of the oxygen-nitrogen bond by a mechanism analogous to the hydrolysis of a carboxylic ester.

The great similarity of the solvolysis of *t*-butyl chloride and of *t*-butyl nitrate, notably the near identity of energy of activation and of the ratio of olefin to alcohol in the reaction product, strongly supports the conclusion of an identity of mechanism. This is, no doubt, the mechanism (2) above, the true solvolysis.

On the other hand, the marked difference in energies of activation of the reactions of benzyl chloride and benzyl nitrate suggests the idea of a materially different mechanism. There is much reason for expecting the reaction of the chloride to partake of both mechanisms (1) and (2), in particular the fact that a strong hydroxyl ion displacement is observed. Since the rates of reaction of nitrate and chloride are nearly the same the entropy of activation must be much greater in the nitrate case than in the chloride.

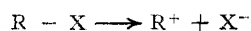
There is evidence that solvolytic reactions of halides which show marked hydroxyl ion displacement reactions and which may therefore be expected to react significantly by mechanism (1) are likely to show smaller entropies of activation than the reactions of halides which go by mechanism (2). Thus benzylidene chloride which shows no measurable hydroxyl ion reaction has an entropy of activation for the solvolytic reaction greater by 11.2 cal./dg. than that of benzyl chloride.^{14a}

It is probably also significant that the entropies of activation of substituted benzyl halides may differ considerably: thus *p*-methylbenzyl chloride has an entropy of activation 6.8 cal./dg. greater than benzyl chloride while *p*-nitrobenzyl chloride has an entropy of activation 1.8 cal./dg. lower.¹⁵

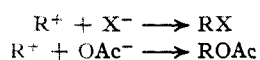
Kinetics of *t*-Butyl Nitrate Solvolysis.—The large dependence of rate on solvent composition

(15) Oliver, *Rec. trav. chim.*, **56**, 247 (1937).

and the characteristic salt effects shown, clearly indicate that tertiary butyl nitrate reacts with water by a true solvolysis. The striking difference between the effects of sodium perchlorate or perchloric acid on one hand and of potassium nitrate, sodium chloride or sodium toluenesulfonate on the other parallels those observed in the hydrolysis of tertiary butyl halides, various benzhydryl halides¹⁶ and benzyl chloride.⁶ If the rate determining step is the ionization



then the rate of reaction will be increased by the presence of electrolyte. This effect is observed in the case of perchlorate ion. The decrease from this rate produced by nitrate, chloride, azide or acetate ion has then been interpreted to mean that some of the carbonium ion was diverted to form either the original ester ("common ion" effect) or a more stable ester.



The marked reduction in rate by hydroxyl ion which we have observed cannot however be explained by any such diversion of the carbonium ion, because attack by hydroxyl ion produces alcohol and would not decrease the rate as measured by acid production. Such an effect is understandable only in terms of a decreased activity on the part of one of the reactants, either water or butyl nitrate. That the effect is through the water, *i. e.*, by way of a varying affinity of the different anions for water molecules, is suggested by the fact that the order of the various ions is approximately that of the Hofmeister series.¹⁷

In an effort to establish their effect on the activity of the water, the freezing points of 60% dioxane containing 0.108 *M* concentration of various solutes were measured in a standard Beckmann freezing point apparatus, the temperature indicated being that of disappearance of sharply defined crystals of dioxane. That the crystallizing phase was dioxane was shown in the case of solvent alone and for the hydroxyl solution by cooling 2–3° below the temperature of first crystals and removing the remaining liquid through a sintered-glass filter under suction. The crystals were melted and distilled free of traces of electrolyte, and the composition measured by refractive

(16) Bateman, Hughes and Ingold, *J. Chem. Soc.*, 960 (1940); Church, Hughes and Ingold, *ibid.*, p. 966; Church, Hughes, Ingold and Taher, *ibid.*, p. 971; Bateman, Church, Hughes, Ingold and Taher, *ibid.*, p. 979.

(17) Traube, *J. Phys. Chem.*, 14, 452 (1910).

index. In both cases the liquid contained more than 80% dioxane. The temperatures in Table XI are average values of four determinations and are probably reliable to ± 0.05 , that for 60% solvent being consistent with data by Hovorka, Schaefer and Dreisbach, for that medium.¹⁸

TABLE XI

FREEZING TEMPERATURE DATA FOR 60% DIOXANE CONTAINING 0.108 *M* CONCENTRATIONS OF ELECTROLYTE

NaOH	-2.70	KNO ₃	-3.92
NaAc	-3.08	Solvent	-4.65
NaCl	-3.35	NaClO ₄	-4.80

For this three-component system at equilibrium the Gibbs–Duhem relationship must hold

$$N_1 d\mu_1 + N_2 d\mu_2 + N_3 d\mu_3 = 0$$

subscript 1 referring to water, 2 to dioxane and 3 to the electrolyte to be added, and for constant ratio N_1/N_2 we may write it in the form

$$N_1 \left(\frac{d\mu_1}{dN_3} \right)_{N_1/N_2} + N_2 \left(\frac{d\mu_2}{dN_3} \right)_{N_1/N_2} + N_3 \left(\frac{d\mu_3}{dN_3} \right)_{N_1/N_2} = 0$$

Since $(d\mu_3/dN_3)$ is positive both $(d\mu_1/dN_3)$ and $(d\mu_2/dN_3)$ might be negative, *i. e.*, both μ_1 and μ_2 might decrease with increasing electrolyte concentration. If, however, one bracketed term can be shown to be positive the other bracketed term must be sufficiently negative to maintain the condition that the sum of the three terms is zero. Since the freezing temperature of the solution with respect to dioxane is raised then the activity of the dioxane in the solution must also be raised, the elevation of the freezing point being a measure of the relative positive value of $(d\mu_2/dN_3)$. In comparing various electrolytes $(d\mu_3/dN_3)$ is approximately a constant and $(d\mu_1/dN_3)$ must vary inversely with $(d\mu_2/dN_3)$. Therefore when the added electrolyte tends to raise the activity of the dioxane component strongly it must act to lower the activity of the water to a corresponding extent.

If the decrease in rate in the presence of hydroxide must be interpreted in terms of such a decrease in the water activity, then the effect of chloride, acetate and nitrate on the freezing point strongly suggests an analogous explanation of their action on the rate of the solvolytic reaction. The data therefore weaken materially the argument of Ingold and Hughes and of Beste and Hammett that direct kinetic evidence exists for a carbonium ion intermediate in the solvolytic reaction.

(18) Hovorka, Schaefer and Dreisbach, *THIS JOURNAL*, 58, 2264 (1936)

Kinetics of the Oxidation-Reduction Reaction.

—Table VII gives the proportion of benzaldehyde formed in the solvolysis of benzyl nitrate, and Table VIII gives the proportion formed in the hydroxyl ion reaction.

The two oxidation-reduction reactions which lead to benzaldehyde and nitrate appear to have the same order as the two hydrolytic ones, although the proportion of benzaldehyde does show some small dependence upon the concentration of hydroxyl ion. In view of the importance recently ascribed to a radical chain mechanism in the Cannizzaro reaction¹⁹ the experiments using "aged" solvent containing large proportions of peroxides are of interest. In the first order reaction the total rate of reaction of benzyl nitrate was unchanged, but the proportion of benzaldehyde produced was approximately doubled. In the reaction with hydroxyl ion the total rate of reaction was materially increased, while the proportion of benzaldehyde decreased slightly if at all.

As was to be expected from the well-known behavior of nitroglycerine and nitrocellulose with alkaline reducing agents, hydroquinone completely suppressed the formation of benzaldehyde in alkaline medium. A similar suppression of aldehyde formation appeared in neutral and acid solutions also. In alkaline media hydroquinone materially increased the total rate of reaction of benzyl nitrate. This suggests some direct attack of hydroquinone or of its ions upon the benzyl nitrate. No such change in the total rate of reaction was observed in neutral or acid solutions.

At the present stage of our knowledge it would seem to be premature to offer any mechanism for the oxidation-reduction reaction.

(19) Weiss, *Trans. Faraday Soc.*, 782 (1941).

Summary

The reactions with water and with sodium hydroxide of *t*-butyl nitrate and of benzyl nitrate have been studied kinetically in various dioxane-water mixtures.

The reaction of *t*-butyl nitrate produces alcohol and olefin in proportions similar to those in which they are formed from *t*-butyl halides. Since, further, the energies of activation of nitrate and halide reactions are nearly identical, an identity of mechanism is strongly indicated. No appreciable reaction with hydroxyl ion or catalysis by acids has been observed.

Although perchlorate ion accelerates, hydroxyl ion retards and other anions have intermediate effects which parallel their effects upon the activity of water in the medium. This materially weakens the direct kinetic argument of Ingold and Hughes and of Beste and Hammett for a free carbonium ion intermediate in solvolytic reactions.

The solvolysis of benzyl nitrate to benzyl alcohol has a much higher energy and entropy of activation than the analogous reactions of benzyl chloride. This suggests that the reaction of the nitrate partakes more largely of a true solvolysis rather than a displacement of anion by water molecule than does that of the halide. There is a pronounced acceleration by hydroxyl ion but acids have no effect.

The conversion of benzyl nitrate to benzaldehyde and nitrite also shows both a kinetically first order reaction of benzyl nitrate and a second order reaction with hydroxyl ion. Both are completely suppressed by the addition of hydroquinone.

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