

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## The Hydration of Isobutene in Dilute Nitric Acid

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While the rate of hydration of isobutene in dilute nitric acid at constant ionic strength is strictly first order with respect to isobutene and oxonium ion, the specific rate constant divided by oxonium ion concentration varies with ionic strength by a factor of 2.64 between ionic strengths of 0.1 and 2.<sup>1</sup> The effect is approximately linear so that the expression for the rate constant can be written in the form

$$k = k' [\text{H}_3\text{O}^+] (1 + k''\mu)$$

and the effect is of unexpected magnitude according to the Brönsted theory of salt effects.<sup>2</sup> Since the ionic strength was varied by the addition of potassium nitrate it is interesting to consider whether the effect can be accounted for in terms of the formation of *t*-butyl nitrate as a transient intermediate. We have investigated this possibility in connection with a recent study of *t*-butyl nitrate hydrolysis in water-dioxane mixtures.<sup>3</sup>

The reaction of an alkyl chloride and mercuric nitrate has been thoroughly investigated and the lack of correspondence between effects on rate and product composition clearly indicates that the reaction occurs by way of a carbonium ion intermediate.<sup>4</sup> We have therefore examined the reaction between *t*-butyl chloride and mercuric nitrate in various dioxane-water mixtures. We have also investigated the effect of the partial substitution of dioxane for water on the rate of reaction of isobutene in dilute nitric acid solutions and established under what conditions *t*-butyl nitrate is found in the reaction product.

### Experimental

**Materials.**—*t*-Butyl chloride (Eastman Kodak Co. best grade) was fractionated, the middle half being taken; b. p. 50.9°. C. P. mercuric nitrate was used directly. The isobutene was prepared by refluxing *t*-butyl alcohol (Eastman best grade) with crystallized oxalic acid<sup>5</sup> and passed through wash bottles containing water and stored over water. When used it was passed from the storage bottle through a long drying tube containing soda lime and calcium chloride. Reagent grade concentrated nitric acid was used in preparing the solutions containing nitric acid. The lithium nitrate was A. C. S. grade recrystallized from water and dried over phosphorus pentoxide.

**Method.**—The method of preparing solutions was that followed in the solvolytic studies of *t*-butyl nitrate.<sup>3</sup> The *t*-butyl chloride was sealed and weighed in tared thin glass bulbs blown from 6-mm. tubing. The procedure was to deliver the approximate amount of the cooled ester into the tared bulb through the 6-mm. neck which was 3–4 inches long; bulb and contents were cooled to dry-ice temperature and the neck sealed quickly in an oxygen flame, preserving the portion of the neck which had been sealed off to be weighed with the sealed bulb. In starting an experiment the reaction bottle containing all the solutes except the ester was placed in the thermostat and brought to temperature equilibrium. The bulb containing the ester was then broken beneath the surface and the initial time taken.

With *t*-butyl chloride Roberts' method of determination of the product ratio by determination of both chloride ion concentration and acidity<sup>4</sup> is unsatisfactory since the hydrolysis of *t*-butyl chloride is appreciable under the conditions of the chloride determination. It was found, however, that the primary reaction between the *t*-butyl chloride and mercuric nitrate producing *t*-butyl alcohol, *t*-butyl nitrate and isobutene is complete within a small fraction of the time required for the subsequent hydrolysis of the *t*-butyl nitrate formed in the reaction. Hence after the preliminary experiments no effort was made to determine the initial slopes, samples being taken at the frequencies previously found satisfactory in the hydrolysis of *t*-butyl nitrate. The reaction was stopped by running a sample into a cold solution of 50% alcohol and 50% dioxane, in which medium lithium chloride was sufficiently soluble to remove the excess mercuric ion, and the titration of acidity was carried out with standard sodium hydroxide using brom phenol blue indicator.

The experiments on the hydration of isobutene were of a semi-quantitative nature since we were interested in the order of magnitude of the rates of reaction in the various media. Into the proper dioxane-water mixture a known volume of dry isobutene gas was bubbled, the acid was added by pipet and the initial time was noted. The sampling was done by a crude modification of the method of Lucas and Ebertz.<sup>1</sup> The end of a pipet similar to the one they used was passed through a two-hole rubber stopper, the other hole containing a short piece of tubing attached to an air bulb. At the time of sampling this rubber stopper was quickly inserted in place of the ground glass stopper of the reaction flask so that the flask was never open for any appreciable time. Pumping the bulb forced the liquid into the pipet until it overflowed and the isobutene concentration was then determined as previously described.<sup>3</sup>

The determination of the amount of *t*-butyl nitrate produced in the hydration reaction offered some difficulty, because the errors in sampling and titration were of the order of the difference between the initial acid titer and that at the time of measurement. The method finally adopted consisted of running the sample into approximately 100 ml. of cold dioxane, adding the approximate amount of 0.1 *N* sodium hydroxide and completing the titration to a

(1) H. J. Lucas and Ebertz, *THIS JOURNAL*, **56**, 460 (1934).

(2) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

(3) G. R. Lucas and Hammett, *THIS JOURNAL*, **64**, 1928 (1942).

(4) Roberts and Hammett, *ibid.*, **59**, 1063 (1937).

(5) Hurd and Spence, *ibid.*, **51**, 2561 (1929).

TABLE I

PRODUCT COMPOSITION IN THE REACTION OF *t*-BUTYL CHLORIDE AND MERCURIC NITRATE IN DIOXANE-WATER MIXTURES

<i>t</i> , °C.	% Dioxane in solvent	Molar concentration of				% Nitrate ester	% Olefin
		BuCl	Hg(NO <sub>3</sub> ) <sub>2</sub>	HNO <sub>3</sub>	LiNO <sub>3</sub>		
0.3	60	0.0245	0.0255	0.0127		6.9	
0.3	60	.0228	.0255	.0126		7.0	
25	75	.0429	.0486	.0239		15.5	5.6
25	75	.0423	.0483	.0238	0.1070	25.6	5.4
25	75	.0249	.0256	.0125		15.4	
25	75	.0206	.0249	.0125	.0985	21.8	
25	85	.0240	.0250	.0126		21.6	
25	95	.0250	.0275	.0138		38.8	
25	95	.0248	.0274	.0138	.0977	58.5	

brom phenol blue end-point with 0.025 *N* sodium hydroxide. The flask was then allowed to warm up and to stand for twenty-four to thirty-six hours. During this period the *t*-butyl nitrate hydrolyzes and titration to a new end-point gives the amount of nitrate ester.

**Rate Calculations.**—The specific rate constant for the disappearance of isobutene was calculated from the first order equation  $\ln a/(a-x) = kt$  where *a* is the initial concentration of the isobutene and (*a* - *x*) is the concentration at time *t*, *t* in seconds.

The fraction of the mercuric nitrate-*t*-butyl chloride reaction product which is *t*-butyl nitrate was determined by a plot of  $\ln(b-x)$  against time, where *b* is the initial concentration of *t*-butyl chloride and *x* is the number of moles reacted as determined by titration at time *t*. That this is actually the plot of the hydrolysis of the *t*-butyl nitrate formed in the reaction was established by comparing the slope of the curve with curves independently determined for *t*-butyl nitrate. The slopes agree within the experimental error. The intercept of the plot at zero time, converted to molar concentration, was used in calculating the per cent. nitrate ester produced. The percentage of olefin formed in the primary reaction between the *t*-butyl chloride and mercuric nitrate was estimated from determinations of the isobutene concentration at several different times early in the run, effort being made not to include any resulting from the hydrolysis of the *t*-butyl nitrate.

### Results

Data for the *t*-butyl chloride-mercuric nitrate reaction are given in Table I. The rates of disappearance of isobutene are given in Table II, together with the amounts of *t*-butyl nitrate appearing in the reaction product.

### Discussion

If we consider the hydration of olefins in dilute nitric acid under conditions where *t*-butyl nitrate

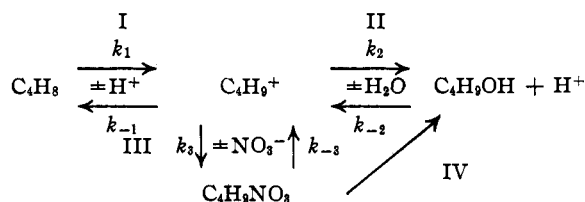
TABLE II

EFFECT OF DIOXANE ON THE RATE OF DISAPPEARANCE OF ISOBUTENE FROM 0.1 *M* HNO<sub>3</sub> AT 25° (TIME IN SECONDS)

Medium	<i>k</i> × 10 <sup>4</sup>	% Nitrate ester found in product
Water	39	None
50% Dioxane	3.3	None
95% Dioxane	0.14	25-30 <sup>a</sup>

<sup>a</sup> In 0.288 *N* HNO<sub>3</sub>.

is formed, the simplest picture we could give would be



In order that the increase in rate of hydration of olefin upon the addition of nitrate ion be explained by the formation of the unstable intermediate, *t*-butyl nitrate, the following conditions must hold

1. Reaction I cannot be the rate determining step —  $k_{-1} \gg k_2$ .
2. To show first order kinetics in respect to isobutene an equilibrium concentration of  $\text{C}_4\text{H}_9^+$  must be maintained —  $k_{-1} \gg k_2$ .
3. Step IV, another route between *t*-butyl nitrate and alcohol, must be postulated.

The rate of reaction in the absence of nitrate ion would then be the relatively slow addition of a water molecule; when nitrate ion is present an alternate path is possible. The linearity of the salt effect on the rate would simply require that  $k_2$  be unaffected by the addition of nitrate ion. Hence

$$k_{\text{H}_3\text{O}^+} = k_{\text{obs.}}/[\text{H}_3\text{O}^+] = k_2 + k_3[\text{NO}_3^-]$$

from which  $k_{\text{H}_3\text{O}^+}$  would be a linear function of the nitrate ion concentration.

Such a theory though plausible is in conflict

with certain experimental facts. The reaction of *t*-butyl chloride with mercuric nitrate, by analogy with the corresponding benzyl chloride system, must occur by way of a carbonium ion. If  $k_{-1} \gg k_2$  then the ratio of olefin to alcohol should be very large. Actually in 75% dioxane the respective percentages of olefin, nitrate and alcohol are shown in Table I to be approximately 5:15:80 where the nitrate ion concentration is 0.014 and 5:25:70 where the nitrate ion concentration is 0.130.

Furthermore the effect of dioxane on the rate of disappearance of olefin seems to be inconsistent with any mechanism involving the combination of isobutene, oxonium ion and nitrate ion to give *t*-butyl nitrate since the rate of such a reaction should be affected by a change in the medium in the same way as is the equilibrium constant of the formation of acetic acid from its ions, which increases markedly with increasing dioxane content.<sup>6</sup>

The amount of *t*-butyl nitrate found in the hydration reaction in 95% dioxane appears to be of the order expected from the product ratio observed in the mercuric nitrate-*t*-butyl chloride reaction and the specific rate constant of hydrolysis of the *t*-butyl nitrate in that medium.<sup>3</sup> If the butyl nitrate did not hydrolyze, upward of 60% of the ester should be produced from the reaction of isobutene as it is in the mercuric nitrate-*t*-butyl chloride reaction. The hydrolysis constant (*i. e.*, the rate of disappearance of *t*-butyl nitrate at unit butyl nitrate concentration) must be at least seventy times as large as the rate at which the substance is formed from isobutene under the prevailing conditions the uncertainty arising from the unknown salt effect. Consequently the value of 25 to 30% nitrate ester observed is of the order expected.

Finally the hydrolysis of *t*-butyl nitrate by its resemblance to that of *t*-butyl chloride appears to be a true solvolytic reaction involving a carbonium ion intermediate<sup>3</sup> and step IV which necessarily by-passes this intermediate is questionable.

(6) Harned and Kazanjian, *THIS JOURNAL*, **58**, 1912 (1936).

Reaction III will therefore ordinarily be significant only under special conditions, *e. g.*, 95% dioxane medium for the hydration reaction, or very rapid formation of carbonium ion as in the *t*-butyl chloride-mercuric nitrate reaction. Hydration of isobutene in water as well as the reaction of mercuric nitrate with *t*-butyl chloride in water would not be expected to produce any nitrate ester because the ratio  $k_2[\text{H}_2\text{O}]/k_3[\text{NO}_3^-]$  clearly increases rapidly with increasing water concentration.

It therefore seems unlikely that the effect of added nitrate ion is due to the formation of *t*-butyl nitrate. In terms of the Brönsted theory of salt effects

$$v = k_0 f_{\text{H}_3\text{O}^+} f_{\text{C}_4\text{H}_9\text{S}}/f_{\text{X}^+}$$

the activity coefficient of the positively charged transition state complex decreases more rapidly than does the product of activity coefficients of the oxonium ion and isobutene. Like effects have been observed in the acid-catalyzed hydration reactions of various ethylene oxides,<sup>7</sup> the acid-catalyzed decomposition of diazoacetic ester<sup>8</sup> and the acid-catalyzed hydrolysis of various acetals,<sup>9</sup> and the effect seems to be general for such reactions.

### Summary

The distribution of products in the reaction of mercuric nitrate with *t*-butyl chloride has been studied in various dioxane-water mixtures. Semi-quantitative results show that the rate of disappearance of isobutene in dilute nitric acid decreases rapidly with increasing proportion of dioxane.

The experimental facts indicate that *t*-butyl nitrate is not an intermediate in the hydration of isobutene in dilute nitric acid, and H. J. Lucas' conclusion that the pronounced acceleration produced by nitrate ion is a salt effect is therefore verified.

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(7) Brönsted, Kilpatrick and Kilpatrick, *ibid.*, **51**, 420 (1929).

(8) Fraenkel, *Z. physik. Chem.*, **60**, 202 (1907).

(9) Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929); Brönsted and Grove, *THIS JOURNAL*, **52**, 1394 (1930).