function of the volume concentration, $c$, over the whole range at 30° and up to 3 molar at 25°. Urea therefore behaves like sucrose and not like typical electrolytes, the apparent molal volumes of which increase linearly with $c^{1/2}$. The experimental results and the partial molal volumes of urea and water are tabulated. Equations giving the apparent molal volume and density as functions of concentration are also included.

The density of solid urea is found to be 1.329 g./ml. at 25° and its molal volume 45.19 ml.

EVANSTON, ILLINOIS RECEIVED AUGUST 1, 1938

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# Kinetics of Neutralization of Pseudo Acids in $H_2O$ and $D_2O$

BY SAMUEL H. MARON[1] AND VICTOR K. LA MER

In this paper are reported kinetic measurements by a conductance method on the neutralization at 0 and 5° of nitromethane, nitroethane, and nitroisopropane by hydroxyl and deuteroxyl ions.

The familiar protolytic processes of ionization and neutralization of acids are in most cases not amenable to kinetic study for they proceed, if not instantaneously, at least with velocities too high to measure. In the class of substances designated as pseudo acids, however, ionization and neutralization proceed at a much slower rate, and in certain cases can be followed kinetically.

This difference in rates of protolytic transfer has been employed by Hantzsch[2] to define a pseudo acid as a substance whose salt formation is a function of time, as against the acid whose neutralization is essentially instantaneous. He states, further, that "if the salt formation is a function of the time, then it is evidence that the molecule undergoes a change in the salt formation process; it is also evidence for the fact that the undissociated substance and its ions are constitutionally different."

As a class, the primary and secondary nitroparaffins have long been recognized as pseudo acids. Ley and Hantzsch[3] have postulated that the primary and rate determining step in the neutralization of a nitroparaffin by a base is the isomerization of the nitro to the aci form, with subsequent rapid neutralization of the latter, *i. e.*

$$\mathrm{RCH_2NO_2 + B \xrightarrow[k_1]{} RCH{=}NOOH + B \xrightarrow[k_2]{} RCH{=}NOO^- + BH^+} \quad (1)$$

and $k_1 << k_2$. In this mechanism the sequence of transformations is nitroparaffin → undissociated aci acid → aci ion. However, Pedersen[4] has shown that this view is inconsistent with present ideas of acid–base catalysis as outlined by Brönsted.[5] The isomerization of a nitroparaffin must be considered a prototropic process, and as such it cannot take place spontaneously, but must involve the intermediary of an acid or basic catalyst. In conformity with this view he actually found the isomerization of nitromethane to the aci form to be a reaction subject to general base catalysis.[4] He consequently postulated as the mechanism of neutralization

$$\mathrm{RCH_2NO_2 + B \xrightarrow[k']{} RCH^-{\cdot}NO_2 + BH^+ \xrightarrow[k']{} RCH{=}NO_2^- + BH^+} \quad (2)$$

*i. e.*, the nitro form donates a proton to the base, and the residue is converted rapidly by an electron shift to the ion. Thus $k_1' << k_2'$, and is rate determining. The aci ion may associate under the proper conditions, to form the aci acid. In this scheme the sequence is nitroparaffin → aci ion → aci acid.

Pedersen's formulation of the mechanism of isomerization of the nitroparaffins has been accepted by Junell,[6] Wynne-Jones,[7] and Reitz,[8] and will be employed to explain the results of this paper.

Following Hantzsch and Veit's[9] orienting semi-quantitative conductivity measurements, Junell[6] studied in $H_2O$ at 0° the neutralization by sodium hydroxide of nitromethane, nitroethane, nitropropane, and nitroisopropane by a modification of

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[1] Present address: Department of Chemical Engineering, Case School of Applied Science, Cleveland, Ohio.

[2] Hantzsch, *Ber.*, **32**, 575–600 (1899).

[3] Ley and Hantzsch, *ibid.*, **39**, 3149 (1906).

[4] Pedersen, *Det. Kgl. Vidensk. Selskab., Math.-fys. Medd.*, **12**, 1–16 (1932) (in English).

[5] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

[6] Junell, (a) *Arkiv Kemi*, **11B**, No. 34 (1934); (b) *Svensk Kem. Tid.*, **46**, 125–136 (1934); (c) Dissertation, Uppsala, 1935.

[7] Wynne-Jones, *J. Chem. Phys.*, **2**, 381–385 (1934).

[8] Reitz, *Z. physik. Chem.*, **A176**, 363–387 (1936).

[9] Hantzsch and Veit, *Ber.*, **32**, 607–627 (1899).

the bromination method. Wynne-Jones, on the other hand, employing a conductance method, studied the neutralization of nitroethane by $Ba(OH)_2$ and $Ba(OD)_2$ at 0° in both light and heavy water.

A reinvestigation of the problem by the conductance method has been undertaken in order: (a) to confirm, refine, and extend Wynne-Jones' measurements, which in heavy water were restricted to a single experiment employing a very small volume of solvent; (b) to ascertain whether the bromination method gives a true measure of the rate of isomerization; (c) to determine the effect of substitution of alkyl groups in the molecule on prototropic rates in light and heavy water; (d) and to determine the rates of proton and deuteron transfer, and their temperature coefficients.

## Experimental

Of the two methods available for following the rates of neutralization of nitroparaffins, conductance is more direct, avoids analytical determinations, and is free of the assumptions of the bromination method. The conductance method depends on the fact that as neutralization proceeds in an equivalent mixture of nitroparaffin and hydroxide, the highly mobile hydroxyl ions are removed, to be replaced by the considerably slower anions of the aci acid formed. Consequently the resistance of the solution increases with time from an initial value, $R_0$, to a final limiting value $R_\infty$, due to the salt of the aci acid. The concentrations and velocity constants can be calculated in terms of the measured resistances.

**Apparatus.**—The bridge employed for measuring resistances was composed of a 1000-cycle microphone hummer, tuned Brown headphones, two variable, 10,000-ohm standard resistance boxes, and an L & N Student Type slide wire. This form of slide wire was preferred to the more accurate Kohlrausch type because balancing and reading could be accomplished with greater speed—an important consideration with the very fast reactions studied.

Four cells differing in size and shape of both cell and electrodes were employed. One was of the Henry type, one of the Freas type, while two were of special design. The latter had a total capacity of 20–25 ml., but required only 2–3 ml. of liquid to cover the electrodes. In these cells measurements could be made with small or large quantities of material; dilutions or additions of reagent could be made with ease. All the runs in $D_2O$ were made in these special cells.

The electrodes were in all cases platinized. No catalytic effect due to the electrodes was observed.

One thermostat consisted of a 12-liter Dewar vessel of large opening, and filled with distilled water and crushed ice. Once charged, and with only occasional manual stirring, the temperature could be kept constant for twenty-four hours. For the experiments at 5° a large capacity water thermostat was operated in conjunction with a refrigerating unit, and regulated to ±0.005°.

**Chemicals.**—The nitromethane and nitroethane were Eastman products, and were purified by repeated fractional distillation. For nitromethane only the fraction boiling at 100.0° at 741.5 mm. was retained, while for nitroethane the fraction boiling at 112.5–113.0° at 739.3 mm. was used.

Nitroisopropane was prepared from purified isopropyl iodide and freshly prepared silver nitrite according to the directions of Kohler.[10] The fraction boiling between 119–120° was collected. Since the product was found to contain nitrous acid, it was treated with urea, dried with calcium sulfate and calcium chloride, and distilled twice under vacuum. The final product was a very mobile, colorless liquid, with a characteristic odor.

The distilled $H_2O$ had a specific conductance of about $1 \times 10^{-6}$ mhos. The $D_2O$, obtained from Hydro Norsk, was purified by molecular distillation under high vacuum twice from alkaline permanganate, and once without any addition. After use the $D_2O$ was freed from organic matter by heating to 60–70° with alkaline permanganate and then distilling several times molecularly *in vacuo*. Water of satisfactory purity could be obtained in this manner without difficulty. Density measurements were made with a 10-ml. pycnometer.

The $Ba(OH)_2$ solution was prepared by dissolving C. P. $Ba(OH)_2 \cdot 8H_2O$, peroxide free, in distilled water. Carbonate was removed by filtration in a closed system through a sintered glass funnel. The $Ba(OD)_2$ was prepared in the same manner by dissolving anhydrous C. P. $Ba(OH)_2$, peroxide free, in $D_2O$, and removing the carbonate by filtration through a micro, all-glass funnel.

The $H_2SO_4$ was prepared by diluting concentrated C. P. acid with distilled water. The $D_2SO_4$ was prepared from thrice recrystallized pyrosulfuric acid and $D_2O$. The recrystallization was accomplished by melting the solid, and allowing part to crystallize.

Both acid and alkali were standardized by titration and on several occasions also gravimetrically as barium sulfate. The $Ba(OH)_2$ and $Ba(OD)_2$ were approximately 0.17 *N*, the acid solutions 0.3 *N*.

**Procedure.**—Since it is difficult to weigh into a cell 1–4 mg. of a volatile liquid with the desired accuracy, stock solutions, 0.04–0.06 *N* in nitroparaffin, were prepared in both light and heavy water. No decomposition in these solutions could be detected after several weeks at 0°.

A definite quantity of solution of the nitroparaffin in $H_2O$ (or $D_2O$) was pipetted into a cell, water added in quantity sufficient to give the desired initial concentration, and the cell placed in the thermostat. The total volumes ranged from 2.4 to 7 cc. for the $D_2O$ and from 5 to 18 cc. for $H_2O$. To initiate reaction an equivalent quantity of $Ba(OH)_2$ [or $Ba(OD)_2$], precooled to the same temperature, was delivered into the cell with a hypodermic syringe; a stop watch was started simultaneously.

Since the reactions are very rapid, and the quantity of reagent to be added in each case was small, 0.15–1.60 cc., it was especially important to deliver the reagent rapidly, with accuracy, and at the same time produce thorough mixing. A set of hypodermic syringes, ranging in capacity from 0.25–2.00 cc., was found to be highly satisfactory

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[10] Kohler, THIS JOURNAL, 38, 898 (1916).

after calibration.[11] When provided with rustless steel or platinum needles these syringes deliver their charge in one to three seconds with a force sufficient to stir the contents of the cell thoroughly. This stirring was supplemented in the initial stages of a run by manual shaking of the cell to eliminate any possibility of concentration differences in the solution.

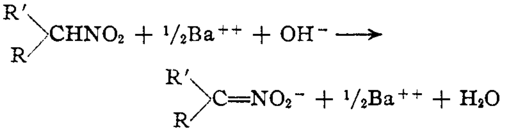
Resistance readings were taken within ten to thirty seconds after the addition of hydroxide. For nitromethane and for nitroethane at 5°, readings were taken at ten-second intervals for the first few minutes, and less frequently thereafter; for nitroisopropane, and for nitroethane at 0°, readings were made at fifteen-second intervals or less frequently, as the occasion demanded. In practically all cases the reaction was followed considerably past the point of half neutralization.

In many of the runs after completion of neutralization the nitroparaffin was regenerated from its barium salt by the addition of an equivalent quantity of sulfuric acid which precipitated the barium and liberated the aci acid. The isomerization of the aci acid to the nitro form is also a time reaction, subject to general acid catalysis.[6b,c] The kinetics of this reaction will be reported in another paper.

Once the nitro form of the pseudo acid had been regenerated, barium hydroxide in equivalent quantity was again added, and the whole sequence of measurements repeated. Thus the reproducibility of the rate and the reversibility of the isomerization process could be established.

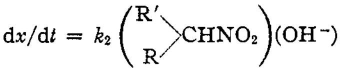
## Results of Measurements

The neutralization of a primary or secondary nitroparaffin by $Ba(OH)_2$ proceeds according to the equation



$$\begin{matrix}R'\\R\end{matrix}\!\!>CHNO_2 + {}^1/_2Ba^{++} + OH^- \longrightarrow \begin{matrix}R'\\R\end{matrix}\!\!>C{=}NO_2^- + {}^1/_2Ba^{++} + H_2O \quad (3)$$

where R and R′ are either a hydrogen atom or an alkyl group. The rate of reaction follows the equations



$$dx/dt = k_2\left(\begin{matrix}R'\\R\end{matrix}\!\!>CHNO_2\right)(OH^-) \quad (4a)$$

$$= k_2\,(a - x)^2 \quad (4b)$$

In terms of resistances it can be shown that Eq. (4b) on integration takes the form

$$k_2 = \frac{1}{at}\left[\frac{R - R_0}{R_\infty - R}\right]\frac{R_\infty}{R_0} \quad (5)$$

where $a$ is the initial concentration of nitroparaffin (and hydroxyl ion), $R_0$ the initial resistance, $R_\infty$ the final, and $R$ the resistance at time $t$.[12]

$R$ and $R_\infty$ in (5) can be measured directly, but $R_0$ must be obtained by extrapolation of the $R$ values to zero time. For rapid reactions, like those of nitromethane and nitroethane, where the resistance increases rapidly with time in the initial stages, it is practically impossible to make such an extrapolation with any certainty or accuracy. Equation (5) can be rearranged to

$$t(R_\infty - R) = \left[\frac{R_\infty}{ak_2R_0}\right]R - \frac{R_\infty}{ak_2} \quad (6)$$

Since for any one experiment the variables are only $t$ and $R$, a plot of $t(R_\infty - R)$ *vs.* $R$ should be a straight line with slope given by

$$\text{slope} = R_\infty/ak_2R_0 \quad (7)$$

and $y$-intercept, $b$

$$b = -R_\infty/ak_2 \quad (8)$$

From the latter $k_2$ follows as

$$k_2 = -R_\infty/ab \quad (9)$$

This method of evaluating $k_2$ was found to be satisfactory, and eliminated the uncertainty in the determination of $R_0$.

In Fig. 1 are shown plots of $t(R_\infty - R)$ *vs.* $R$ for nitroethane and nitroisopropane in $H_2O$ and in $D_2O$. The linear character of the plot furnishes evidence of the fidelity with which equation (6), and hence equation (4), reproduces the data in a given experiment.

The results obtained with nitromethane, nitroethane, and nitroisopropane in both light and heavy water are summarized in Tables I, II and III. The A runs refer to the first neutralization of the nitroparaffin; the B runs are those made with nitroparaffin which had been neutralized, reconverted to the nitro form, and again neutralized. Because of its high rate, the neutralization of nitromethane was measured only at 0° in light water. Nitroethane has been studied at both 0 and 5° in light water and at 5° in heavy water. Only once were we fortunate in maintaining supercooling to obtain a measurement at 0° in heavy water; in five subsequent attempts the supercooled $D_2O$ solutions froze and made rate measure-

TABLE I

THE NEUTRALIZATION OF NITROMETHANE IN $H_2O$ AT 0°

| Run | Concn., equiv. l. | $k_2$ |
|---|---|---|
| 43-A | 0.00693 | 235.1 |
| 41-A | .00489 | 240.1 |
| 40-A | .00451 | 237.2 |
| 44-A | .00306 | 238.1 |
| 44-B | .00298 | (254.2) |
| | | 237.6 ± 1.5 |
| | | ± 0.63% |

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[11] The syringes, manufactured by Becton, Dickinson & Co., Rutherford, N. J., were of the Tuberculin or Precision type. The 0.25-cc., the 0.50-cc., and the 1.00-cc. syringes were subdivided into 0.01 cc., and could be estimated further to 0.001, 0.002, and 0.003 cc., respectively. The 2.00-cc. syringe was subdivided into 0.05 cc. and could be read easily to 0.01 cc.

[12] Wynne-Jones[7] gives this equation without proof. We find that in order to derive this expression it is necessary to assume that the *specific* conductances of the ionic species present in solution are additive and that they vary linearly with concentration.

ments impossible at that temperature. Consequently nitroisopropane has been studied at 0 and 5° in light water, and only at 5° in $D_2O$.

TABLE II

THE NEUTRALIZATION OF NITROETHANE IN $H_2O$ AND $D_2O$

| Solvent | Temp., °C. | Run | Concn. | $k_2$ |
|---|---|---|---|---|
| $H_2O$ | 0.00 | 8-A | 0.0419 | 38.43 |
| | | 26-A | .0415 | 39.02 |
| | | 7-A | .0329 | 39.03 |
| | | 26-B | .0299 | 39.32 |
| | | 6-A | .0283 | 39.50 |
| | | 7-B | .0251 | 38.88 |
| | | 23-A | .0237 | 39.53 |
| | | 22-A | .0237 | 39.32 |
| | | 24-A | .0236 | 39.33 |
| | | 24-B | .0193 | 39.23 |
| | | 6-B | .0168 | 38.60 |
| | | | | 39.11 ± 0.29 |
| | | | | ± .74% |
| $H_2O$ | 5.00 | 53-A | .0310 | 57.88 |
| | | 51-A | .0273 | 58.57 |
| | | 54-A | .0244 | 58.27 |
| | | 50-A | .0200 | 59.20 |
| | | 50-B | .0157 | 58.84 |
| | | 52-A | .0120 | 57.46 |
| | | | | 58.37 ± 0.50 |
| | | | | ± .86% |
| | | First stage | | |
| 99.3% $D_2O$ | 0.00 | 45-A | 0.0266 | 55.6 |
| 99.1% $D_2O$ | 5.00 | 46-A | .0266 | 81.69 |
| | | 56-A | .0201 | 81.95 |
| | | 57-A | .0175 | 81.00 |
| | | 58-A | .0155 | 80.69 |
| | | | | 81.33 ± 0.49 |
| | | | | ± .60% |
| | | Second stage | | |
| 99.3% $D_2O$ | 0.00 | 45-B | 0.0207 | 20.7 |
| 99.1% $D_2O$ | 5.00 | 46-B | .0207 | 29.82 |
| | | 48-B | .0169 | 29.58 |
| | | 56-B | .0169 | 29.54 |
| | | 57-B | .0150 | 29.21 |
| | | | | 29.54 ± 0.16 |
| | | | | ± .54% |

Attention should be directed to the B runs in Table II. The results of these runs are evidence that the barium salt of nitroethane is stable, and that it can be reconverted *completely* to the nitro form by the addition of an equivalent quantity of sulfuric acid. The same can be said for Run 44-B in Table I. Although the result deviates from the mean, still it must be considered as satisfactory evidence, if the uncertainties of reagent addition, barium sulfate precipitation, and the high rate of the reaction be recognized.

No B runs could be made with nitroisopropane. Although the barium salt was stable, the free acid, liberated on addition of an equivalent quantity of sulfuric acid, decomposed partially to yield a

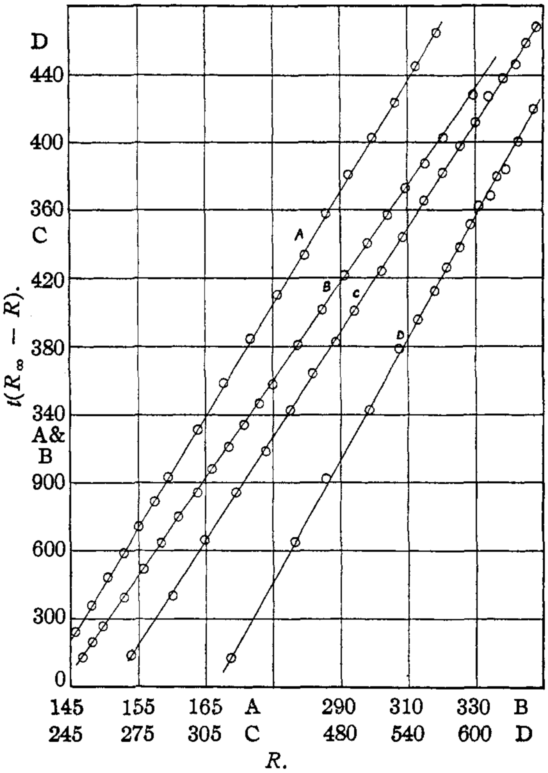

Fig. 1.—Plot of $t(R_\infty - R)$ *vs.* $R$ at 5°: A, 0.0168 $N$ nitroisopropane in $H_2O$; B, 0.0245 $N$ nitroisopropane in $D_2O$; C, 0.0273 $N$ nitroethane in $H_2O$; D, 0.0266 $N$ nitroethane in $D_2O$.

TABLE III

THE NEUTRALIZATION OF NITROISOPROPANE IN $H_2O$ AND $D_2O$

| Solvent | Temp., °C. | Run | Concn. | $k_2$ |
|---|---|---|---|---|
| $H_2O$ | 0.00 | 30-A | 0.0349 | 2.08 |
| | | 31-A | .0301 | 2.08 |
| | | 32-A | .0265 | 2.05 |
| | | 33-A | .0213 | 2.08 |
| | | 34-A | .0165 | 2.09 |
| | | | | 2.08 ± 0.01 |
| | | | | ± .48% |
| $H_2O$ | 5.00 | 61-A | .0307 | 3.36 |
| | | 64-A | .0263 | 3.37 |
| | | 62-A | .0231 | 3.38 |
| | | 65-A | .0206 | 3.35 |
| | | 66-A | .0168 | 3.34 |
| | | 63-A | .0116 | 3.34 |
| | | | | 3.36 ± 0.01 |
| | | | | ± .30% |
| 99.1% $D_2O$ | 5.00 | 69-A | .0359 | 4.62 |
| | | 67-A | .0310 | 4.59 |
| | | 68-A | .0245 | 4.57 |
| | | 70-A | .0150 | 4.54 |
| | | | | 4.58 ± 0.03 |
| | | | | ± .66% |

TABLE IV

SUMMARY AND COMPARISON OF RESULTS IN $H_2O$

| Substrate | Temp., °C. | $k_1$<br>Maron and La Mer (cond.) | Junell (brom.) | Wynne–Jones (cond.) |
|---|---|---|---|---|
| Nitromethane | 0 | 237.6 ± 1.5 | 171 ± 3 | .. |
| Nitroethane | 0 | 39.11 ± 0.29 | 35.2 ± 1.0 | 39.0 ± 2.0 |
| | 5 | 58.37 ± .50 | .. | .. |
| Nitropropane | 0 | .. | 29.2 ± 0.2 | .. |
| Nitroisopropane | 0 | 2.08 ± .01 | 1.94 ± .04 | .. |
| | 5 | 3.36 ± .01 | .. | .. |

product or products other than the nitro form. In this respect Junell's[6c] (p. 110) experience is in accord with our own.

The nitroethane measurements in $D_2O$ merit further explanation. Wynne-Jones[7] first called attention to the fact that it should be possible to study the kinetics of exchange of the H for D atoms on the carbon adjacent to the nitro group in nitroethane by the following series of reactions carried out in $D_2O$

$$CH_3CH_2NO_2 + OD^- \xrightarrow{k_1} CH_3CH{=}NO_2^- + HOD \qquad (10a)$$

$$CH_3CH{=}NO_2^- + D_3O^+ \longrightarrow CH_3CHDNO_2 + D_2O \qquad (10b)$$

$$CH_3CHDNO_2 + OD^- \xrightarrow{k_2} CH_3CD{=}NO_2^- + HOD \qquad (11a)$$

$$CH_3CD{=}NO_2^- + D_3O^+ \longrightarrow CH_3CD_2NO_2 + D_2O \qquad (11b)$$

$$CH_3CD_2NO_2 + OD^- \xrightarrow{k_3} CH_3CD{=}NO_2^- + D_2O \qquad (12a)$$

The idea in this sequence of reactions is to remove the protons one at a time with $OD^-$ and introduce deuterons instead of protons with $D_3O^+$, until finally only D atoms are attached to the alpha carbon. Further neutralization should involve the transfer of a deuteron to the $OD^-$ ion (12a). By this simple artifice it should be possible to measure both the rate of proton transfer (10a) and deuteron transfer (12a) to the same ion, $OD^-$, in the same solvent $D_2O$. Reaction (11a) would proceed only as written if the rate of proton removal is considerably greater than that of the deuteron from $CH_3CHDNO_2$.

One such sequence of measurements with nitroethane was carried out by Wynne-Jones at 0°. We have repeated these experiments at both 0 and 5°. In Table II the constants designated first stage refer to reaction (10a), while those marked second stage refer to reaction (11a). Stage three, corresponding to (12a), could not be measured for reasons to be given below.

## Comparison of Results with Previous Measurements

In Table IV are summarized all the known rate constants for the neutralization of nitroparaffins in light water. Inspection of these data shows that Wynne-Jones' result for nitroethane at 0° is in very good agreement with our value of 39.11. On the other hand, Junell's constants, obtained by a bromination method, are in every case *lower* than those of this paper.

The conductance method measures directly the rate of removal of hydroxyl ions from solution. Since the latter are removed in the reactions under discussion by taking on a proton from the substrate, we conclude that we are measuring directly the rate of proton transfer to hydroxyl ions. In the bromination method, however, the rate of proton transfer is arrived at indirectly through two fundamental assumptions. As used by Junell, the procedure consisted in neutralizing a nitroparaffin with sodium hydroxide up to a certain point, and then suddenly adding a large excess of strongly acid solution of bromine. The assumptions were (1) that the acid would neutralize the alkali and thus stop the reaction, and (2) that the bromine would react very rapidly with the aci acid present. From the quantity of bromine consumed the extent of neutralization at the time of addition of bromine could then be calculated.

Nothing definite can be said about the second of these assumptions. It is known that bromine is absorbed very rapidly by the aci form of a nitroparaffin, but just how rapidly is still an open question. To the first assumption, however, two serious objections can be raised. First, Nef[13] has shown that in the presence of excess mineral acid the aci salts are unstable and decompose to give various products. Secondly, Junell[14] has shown that in the presence of $H_3O^+$ the anions of the aci-paraffins isomerize rapidly to the nitro-forms.

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[13] Nef, *Ann.*, **280**, 263–291 (1894).

[14] Refs. 6b; 6c, p. 79.

He has shown, further, that the reaction anion + acid is subject to general acid catalysis. We may expect that even with a very rapid bromination rate, an appreciable back reaction may set in on addition of a large excess of mineral acid, converting some aci to nitro-form before bromination is completed. The two factors mentioned should operate to give *low* results for the concentration of aci form, and hence for $k_2$. The error should be especially large with nitromethane, where the rate constant for the back reaction is known to be large, and smaller for the other nitro-paraffins under discussion.

This is actually the case, as may be seen from Table IV. The divergence between the rate constants of this paper and Junell's is 28% for nitromethane, about 10% for nitroethane, and about 7% for nitroisopropane.

It should be mentioned that Junell, in some preliminary experiments, tried out his method on nitroethane and found the error involved in the concentration determinations to be 0.5–4%, depending on the dexterity of operation. The error in the determination of the nitromethane concentrations would then be expected to be even larger, leading to greater error in the constants for nitromethane. These facts substantiate the above analysis of the bromination procedure.

In view of these considerations we consider the results of conductance to be more accurate and reliable than those obtained by the bromination method.

Table V gives a summary and comparison of the kinetic constants obtained in $D_2O$. The agreement between Wynne-Jones' value at 0° for the first stage and that of this paper is fair, but there is no agreement at all for the second. Wynne-Jones' $k_2 = 36$ is altogether too high in view of the constants measured at both 0 and 5°. For the third stage Wynne-Jones reported a rather unsatisfactory constant varying from 6 to 15. We have found that no satisfactory constants for this stage can be obtained because the $CH_3CD{=}NOO^-$ ion, although stable in the salt, is more sensitive to acid than the corresponding $CH_3CH{=}NOO^-$ ion, and undergoes some decomposition on addition of $D_2SO_4$. In the light of Nef's[13] work the decomposition product may be expected to be $CH_3CDO$. A test with 2,4-dinitrophenylhydrazine gave a positive reaction. This finding renders Wynne-Jones' measurement of the third stage too questionable to have any meaning in the calculation of ratio of proton to deuteron transfer.

TABLE V

COMPARISON OF RESULTS FOR NITROETHANE IN $D_2O$

| | Temp., °C. | $k_2$ | |
|---|---|---|---|
| | | Maron and La Mer | Wynne-Jones |
| First stage | 0 | 55.6 | 60 |
| | 5 | 81.33 ± 0.49 | .. |
| Second stage | 0 | 20.7 | 36 |
| | 5 | 29.54 ± .16 | .. |
| Third stage | 0 | No result | 6–15 |

## Discussion

The rate of proton donation by a nitroparaffin to a base depends greatly on the nature of the atoms or groups attached to the $\alpha$-carbon. An inspection of Table IV shows that the rate of neutralization is highest for nitromethane and least for nitroisopropane, *i. e.*, the greater the number of hydrogen atoms attached to the $\alpha$-carbon the greater the rate of proton donation to a base. As the hydrogens are progressively replaced by alkyl groups, the rate decreases rapidly. Apparently the length of the substituent alkyl group is of relatively minor importance, since the rates of neutralization of nitroethane and *n*-nitropropane are not very different. On the other hand, the number of alkyl substituents is of importance, as is evidenced by the very large decrease in rate constants when two hydrogen atoms are replaced by methyl groups in nitroisopropane.

Qualitatively these observations are in accord with the "inductive effect" ascribed to methyl groups in particular and to alkyl groups in general. An alkyl group is considered to be more "electron repulsive" than a hydrogen atom. Consequently, on replacement of a hydrogen atom by an alkyl group, the carbon to which the attachment is made becomes more negative by induction, and exercises a greater attraction for the proton. This stronger attraction between hydrogen and carbon should be evidenced by a decrease in rate beyond that expected on purely statistical grounds. Such is actually the case. From Table IV it will be observed that the rate inhibiting effect of various alkyl groups is in the order

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right> > CH_3CH_2 > CH_3 > H$$

This is the sequence found by Kharasch and Flenner[15] for the order of increasing electron repulsive character of alkyl groups, and is also the order

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[15] Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

given by Watson[16] for the relative magnitudes of the "inductive effect."

Again, the inductive influence of halogen, which is electron attractive, should be to increase the rate of prototropic change. This is in accord with Junell's measurements[17] which show that the rates of ionization of brominated nitromethane and nitroethane are faster than those of the corresponding unhalogenated nitroparaffins.

Quantitatively, the velocity constants for the neutralization of nitroisopropane, *n*-nitropropane, nitroethane and nitromethane are in the ratio 1:14:18:114, respectively. These figures are not explicable on purely statistical grounds. Again, the effect of the methyl groups is not additive. Although there is about a six-fold decrease in rate on going from nitromethane to nitroethane, the decrease in rate from nitroethane to nitroisopropane is 18-fold. These variations in rate, outside of statistical considerations, can be ascribed only to differences in force of binding of the hydrogen to the carbon produced from compound to compound by the substitution of alkyl groups.

The heavy water experiments add nothing to the above facts. The ratio of the velocity constants of nitroethane to nitroisopropane in $D_2O$ is the same as in $H_2O$, 18. These experiments do show, however, that the rate of proton transfer from a nitroparaffin to $OD^-$ in $D_2O$ is *faster* than the rate for the transfer of a proton to $OH^-$ in $H_2O$. The ratio of velocity constants is essentially constant, being 1.42 and 1.39 for nitroethane at 0 and 5° and 1.36 for nitroisopropane at 5°. Such accelerations in reactions involving $OH^-$ and $OD^-$ ions in the two media have been observed in the saponification of ethyl acetate,[18] the hydrolysis of diacetone alcohol,[19] and the hydrolysis of the monochloroacetate ion.[20] The ratios found there were in the order given 1.33, 1.22 (15°) and 1.2 (45°).

Since the substrates in the examples cited were the same in both $H_2O$ and $D_2O$, the differences in rate in the two media may be ascribed to solvent effect and to differences in the $OH^-$ and $OD^-$ ions. It is doubtful whether the solvent alone would account for a 40% acceleration in rate observed here. These experiments indicate that the $OD^-$ ion is a stronger base than the $OH^-$ ion, and by virtue of its greater basicity accelerates the rate of proton removal from the substrate.

The ratios of the rates of proton to deuteron transfer could not be determined by the method suggested by Wynne-Jones. Nor do the results for the first and second stages for nitroethane in $D_2O$ support Wynne-Jones' contention that the rate of removal of a proton from $CH_3CH_2NO_2$ is essentially twice that from $CH_3CHDNO_2$. This factor of two was explained on statistical grounds by the decrease in number of mobile protons present from two to one. His conclusion was based on a value of $k_2 = 36$ for the second stage, a value we believe to be considerably in error. The results of this paper show that the ratio of constants in the first and second neutralization stages is 2.7. There is no evidence for a simple quantitative statistical connection between rate constants and number of prototropic hydrogens in the molecule.

The rate constants reported in Tables II and III can be expressed as functions of the temperature by the equations

(a) Nitroethane in $H_2O$

$$\log_{10}k = -\frac{2640.5}{T} + 11.261$$

(b) Nitroethane in $D_2O$, first stage

$$\log_{10}k = -\frac{2513.7}{T} + 10.949$$

(c) Nitroethane in $D_2O$, second stage

$$\log_{10}k = -\frac{2341.0}{T} + 9.888$$

(d) Nitroisopropane in $H_2O$

$$\log_{10}k = -\frac{3163.0}{T} + 11.899$$

The units are equivalents per liter and minutes.

Columns (4) and (5) of Table VI summarize the energies of activation and the constant $B$ in the Arrhenius equation: $\log_{10}k = B - (\Delta E^*/2.303RT)$. All the reactions proceed with energies of activation somewhat lower than are usually encountered (*ca.* 20,000 cal.). The considerably lower rate for nitroisopropane in $H_2O$ as compared with nitroethane in the same solvent is partially explicable by the difference of 2400 cal. in the energies of activation. The increase in rate of neutralization of nitroethane in $D_2O$ over that in $H_2O$ may be accounted for by the decrease in energy of activation of 600 cal. although this difference would call for a larger increase in rate than has been observed. However, no explanation can be advanced on this basis for the rate observed in the second stage for nitroethane in

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[16] Watson, "Modern Theories of Organic Chemistry," Oxford University Press, New York, 1937, p. 74.

[17] Junell, *Z. physik. Chem.*, **A141**, 71–90 (1929).

[18] Wynne-Jones, *Chem. Rev.*, **17**, 117 (1935).

[19] Hornel and Butler, *J. Chem. Soc.*, 1361–1366 (1936).

[20] Reitz, *Z. physik. Chem.*, **A177**, 85–94 (1936).

TABLE VI

ENERGIES AND ENTROPIES OF ACTIVATION

| (1) Substrate | (2) Solvent | (3) Log $\frac{k_5^\circ}{k_0^\circ}$ | (4) $\Delta E^*$, cal. | (5) $B$ min.$^{-1}$ | (6) Log $k$ (2.5°) | (7) $\frac{-\Delta E^*}{2.303RT}$ | (8) $\frac{\Delta S^*}{2.303R}$ | (9) $\Delta S^*$ |
|---|---|---|---|---|---|---|---|---|
| Nitroethane | $H_2O$ | 0.1738 | 12,100 | 11.26 | 1.70 | − 9.58 | −3.26 | −14.99 |
| Nitroethane | | | | | | | | |
| First stage | $D_2O$ | .1655 | 11,500 | 10.95 | 1.83 | − 9.12 | −3.59 | −16.41 |
| Second stage | $D_2O$ | .1541 | 10,700 | 9.89 | 1.40 | − 8.49 | −4.65 | −21.25 |
| Nitroisopropane | $H_2O$ | .2082 | 14,500 | 11.90 | 0.42 | −11.48 | −2.64 | −12.06 |

$D_2O$. Although the energy of activation is lower than that for the first stage by about 800 calories the rate observed is also lower, though the exact opposite would be expected. The difficulty can be resolved by ascribing a part of the difference in rates observed to differences in entropy of activation of the reactions in question. The magnitude and variations in the $B$ constant show that the entropy terms are appreciable.

According to the transition state theory of reaction velocity[21]

$$k = \frac{RT}{Nh} e^{-\Delta S^*/R} e^{-\Delta E^*/RT} \qquad (13)$$

or

$$\log_{10}k = \log_{10}\frac{RT}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta E^*}{2.303RT} \qquad (14)$$

where $R/N$ and $h$ are the Boltzmann and Planck constants, respectively, and $\Delta S^*$ is the entropy of activation for all degrees of freedom.[22] By comparison with the Arrhenius equation

$$B = \log_{10}\frac{RT}{Nh} + \frac{\Delta S^*}{2.303R} \qquad (15)$$

Since $\Delta E^*$ was taken as constant for 0 and 5° in the calculation of $B$, $\Delta S^*$ values were calculated for the average temperature of 2.5°. At this temperature $\Delta S^*$ is given by

$$\frac{\Delta S^*}{2.303R} = B - \log_{10}\frac{RT}{Nh} = B - 14.54 \qquad (16)$$

when the time is expressed in minutes. The values are tabulated in columns (8) and (9) of Table VI, and show large negative values for the entropy of activation.

Columns (7) and (8) give the activation energy and activation entropy contributions to the logarithm of the velocity constant at 2.5° shown in column (6). The entropy contributions are in every case large fractions of the energy contributions. Comparison of nitroethane and nitroisopropane in $H_2O$ shows that the decrease in rate observed for nitroisopropane is due primarily to increase in activation energy,[23] although an increase in the activation entropy of about three units mitigates the decrease in rate constants. On the other hand, the increase in rate in $D_2O$ over that in $H_2O$ for nitroethane is due to the fact that although the entropy decreases, the simultaneous decrease in the energy of activation outweighs the effect of the entropy, thus leading to a higher rate of reaction. For the second stage, however, just the reverse is true. Here the decrease in entropy of activation outweighs considerably the decrease in the activation energy, and consequently the rate constants *decrease* although from a consideration of activation energies alone they should increase.

## Summary

1. The rates of neutralization of nitromethane, nitroethane, and nitroisopropane by $OH^-$ ion in $H_2O$ and by $OD^-$ ion in $D_2O$ have been studied by a conductance method. Measurements are given for nitromethane at 0° in $H_2O$ and for nitroethane and nitroisopropane at 0 and 5° in both $H_2O$ and $D_2O$.

2. The rate constants for these prototropic reactions in $H_2O$ decrease as we pass from nitromethane to nitroethane, to nitroisopropane. A qualitative explanation of this change in rate with substitution is given in terms of the "inductive effect" of alkyl groups.

3. The rates for nitroethane and nitroisopropane are 40% faster in $D_2O$ than in $H_2O$ at the same temperature.

4. The results of this paper have been compared with previous measurements in the light of

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[21] Wynne-Jones and Eyring, *J. Chem. Phys.*, **3**, 492 (1935); Eyring, *Chem. Rev.*, **17**, 65 (1935).

[22] La Mer and Liotta, THIS JOURNAL, **60**, 1967 (1938); La Mer, *J. Franklin Inst.*, **225**, 709 (1938). See p. 729 for a more detailed discussion of difference between the entropy of activation as defined by Eyring ($\Delta S^*$) and as defined by La Mer ($\Delta S_{\text{act.}}$) in *J. Chem. Phys.*, **1**, 289 (1933).

[23] By the term "increase in activation entropy" on passing from nitroethane to nitroisopropane we refer to the algebraic increase in the entropy of the activation process: $S^* = -15$ to 12 E. U. respectively. This means that the latter complex is more probable, *i. e.*, more states, in the statistical sense, exist for the isopropane than for the ethane complex. On the other hand the energy differences for the activation process represented by $\Delta E^*/2.3RT$ are higher for the former, namely, 11.48 and 9.58. Hence the rate of reaction is slower for nitroisopropane.

the methods employed. A critical discussion of the bromination method is given, and certain errors pointed out.

5. Wynne-Jones' attempt to determine the ratio of proton to deuteron transfer by progressive exchange of H for D in nitroparaffins is inapplicable to nitroethane and nitroisopropane because of the instability of the substrate at certain stages in the process.

6. Equations for rate constants as functions of temperature are given, and energies and entropies of activation calculated. It is shown that the differences in rates observed cannot be explained in terms of changes in the activation energy alone; the differences in the observed rates are caused by an interplay of variations in both energy and entropy of activation.

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[CONTRIBUTION NO. 362 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

# Reactions of Trialkyl Phosphates, Alkyl Acetates, and Tertiary Butyl Hypochlorite in the Friedel-Crafts Syntheses[1]

BY NATHAN BERMAN AND ALEXANDER LOWY

The synthesis of alkylated substances by means of the Friedel-Crafts reaction has been extended widely from the original use of alkyl chlorides with aromatic hydrocarbons. An important advance in the alkylation reaction was the application of esters to the synthesis. Among the esters used were: alkyl borates, alkyl acetates, alkyl formates, *n*-butyl oxalate, tetraethyl silicate, and diethyl carbonate. The trialkyl phosphates gave phenol ethers with phenol.

The purpose of this investigation was to observe whether the use of esters might be extended to the alkyl esters of phosphoric acid, acetic acid, and tertiary butyl hypochlorite. These substances proved to be efficient alkylating agents. The conditions which influenced the yield of alkylated benzenes were observed, such as concentration of reagents, duration of heating, and reaction time.

## Experimental

The apparatus employed for the alkylations was the usual one-liter three-necked Pyrex flask, into one neck of which extended a dropping funnel and thermometer. The central neck was fitted with a glass stopper and mercury seal, through which extended a motor-driven glass stirrer. The third neck was connected to a modified Hopkins-type reflux condenser. Fractionations were conducted with a seventeen-inch (43-cm.) Vigreux column, which was wrapped in asbestos paper.

The aluminum chloride used throughout was of 99.5% purity. The benzene was dried over sodium and distilled at 80–81°. The various esters were purified by distillation or by vacuum distillation before use.

**Typical Experiment. Triethyl Phosphate.**—Benzene (435 g.) was stirred with 68.5 g. (0.515 mole) of aluminum chloride in the Pyrex flask, surrounded by an ice-water bath; 25 g. (0.137 mole) of triethyl phosphate was added dropwise through a separatory funnel over a two-hour period. The mixture was then stirred for eight hours at room temperature (20–25°). Throughout this time there was a vigorous evolution of hydrogen chloride. The mixture was poured over cracked ice and allowed to hydrolyze overnight. The benzene layer was washed with aqueous sodium bicarbonate and water, dried over calcium chloride, filtered, and fractionally distilled. There was obtained 27 g. of ethylbenzene boiling at 134–137°; $n^{20}\text{D}$ 1.4951. There was also obtained 8 g. of a higher boiling fraction.

**Preparation of Triisopropyl Phosphate.**—The procedure analogous to that described in "Organic Syntheses" for the preparation of *n*-butyl phosphate[2] was followed. In the four-necked flask fitted with (a) a mercury-sealed stirrer, (b) a Hopkins-Cole type condenser, (c) a thermometer, and (d) a separatory funnel, there was mixed three moles (180 g.) of isopropyl alcohol with 3.3 moles of pyridine and 275 ml. of benzene as solvent. This mixture was stirred and cooled in an ice-salt bath to −5°. Through the separatory funnel, 153 g. of phosphorus oxychloride was added dropwise over six hours at such a rate that the temperature never exceeded 10°. The mixture was refluxed for two hours at 80°; 500 ml. of water was added to dissolve the pyridine hydrochloride; the benzene layer was washed with 100 ml. of water and dried over anhydrous sodium sulfate. On vacuum distillation, 100 g. of triisopropyl phosphate was collected, which represents a 44.7% yield. Its boiling point was 122–125°, at 15–16 mm. pressure.

The accompanying Table I gives the results of the experiments conducted with the various esters as alkylating agents. The experimental procedure was analogous to that followed in the experiment with triethyl phosphate, except as indicated below.

I. Alkylating agent = triethyl phosphate (b. p. 96–101° at 3–5 mm.). Product = ethylbenzene (b. p. 134–137°; $n^{20}\text{D}$ 1.4951).

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[1] Abstracted from a thesis presented by Nathan Berman to the Graduate School in partial fulfilment of the requirements for the Ph.D. degree.

[2] *Org. Syntheses*, **16**, pp. 9–12 (1936).