TABLE III

MASS SPECTRUM OF BUTENE-1

| $m/e$<br>$V^-$ | 56<br>$C_4H_8^+$ | 55<br>$C_4H_7^+$ | 54<br>$C_4H_6^+$ | 53<br>$C_4H_5^+$ | 52<br>$C_4H_4^+$ | 51<br>$C_4H_3^+$ | 50<br>$C_4H_2^+$ | 49<br>$C_4H^+$ | 48<br>$C_4^+$ |
|---|---|---|---|---|---|---|---|---|---|
| 20 | 100 | 30.5 | 2.6 | 2.1 | ... | .. | .. | ... | ... |
| 30 | 117 | 53.0 | 6.0 | 11.4 | 1.5 | 2.5 | 0.7 | ... | ... |
| 40 | 122 | 59.0 | 7.0 | 14.9 | 3.3 | 8.4 | 5.7 | ... | ... |
| 50 | 127 | 61.1 | 7.2 | 15.4 | 3.6 | 10.5 | 10.1 | 2.0 | 0.2 |
| 60 | 130 | 64.0 | 7.3 | 15.8 | 3.6 | 11.0 | 11.4 | ... | ... |

| $m/e$<br>$V^-$ | 42<br>$C_3H_6^+$ | 41<br>$C_3H_5^+$ | 40<br>$C_3H_4^+$ | 39<br>$C_3H_3^+$ | 29<br>$C_2H_5^+$ | 18<br>$C_2H_4^+$ | 27<br>$C_2H_3^+$ | 26<br>$C_2H_2^+$ | 15<br>$CH_3^+$ | 14<br>$CH_2^+$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 20 | 3.9 | 153 | 8.2 | 12.0 | .. | .. | .. | .. | .. | ... |
| 30 | 5.2 | 275 | 17.7 | 66.0 | 34 | 71 | 41 | 4.5 | 3.2 | ... |
| 40 | 5.2 | 320 | 21.0 | 91.1 | 47 | 95 | 85 | 16.5 | 7.6 | ... |
| 50 | 5.2 | 335 | 22.1 | 98.0 | 48 | 97 | 95 | 24.5 | 9.6 | 2.9 |
| 60 | ... | ... | 22.8 | 99.1 | 49 | 98 | 99 | 28.0 | 10.4 | 3.7 |

The relative abundances have been corrected for the presence of $C^{13}$ in its natural abundance of 1.1%. The dots indicate no measurement was made.

8.0%, $i$-$C_4H_{10}$ 4.3%, $l$-$C_4H_8$ 12.7% and $i$-$C_4H_8$ 14.7%. This comparison is specifically for 50 volt electrons, but it holds approximately for bombardment by electrons of from 30 to 100 volts energy. It will be noted that the unsaturates have considerably less tendency to dissociate after ionization by electron impact than do the saturates.

## Summary

The appearance potentials and relative abundances of a large portion of the ions in the mass spectrum of butene-1 are reported. The vertical ionization potential of butene-1 is found to be $9.6_5 \pm 0.1$ e. v., 0.8 e. v. higher than that of isobutylene. The heat of dissociation of the $C_2H_5$—$C_2H_3$ bond is $3.3_0 \pm 0.2$ e. v. and the ionization potential of the vinyl radical is $9.8_7 \pm 0.2$ e. v. The mass spectrum of butene-1 is briefly compared with those of isobutylene and the butanes. A summary of the heats of dissociation deduced from electron impact data is included.

E. PITTSBURGH, PA. RECEIVED NOVEMBER 9, 1942

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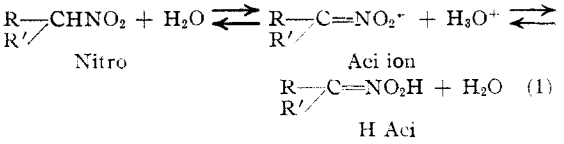
[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

# The Ionization Constants of Aci and Nitro Forms of Some Nitroparaffins

BY DAVID TURNBULL AND SAMUEL H. MARON

It is well known that nitroparaffins possessing a hydrogen atom on the $\alpha$-carbon exist in two tautomeric forms, nitro and aci, both of which exhibit acidic properties. The anions produced in the ionization of the two forms are apparently indistinguishable. The ionization equilibria involved can be represented in general by the equations



$$\underset{\text{Nitro}}{RR'CHNO_2} + H_2O \rightleftharpoons \underset{\text{Aci ion}}{RR'C{=}NO_2^-} + H_3O^+ \rightleftharpoons \underset{\text{H Aci}}{RR'C{=}NO_2H} + H_2O \quad (1)$$

where R and R′ may be either hydrogen atoms or alkyl groups. According to the evidence deduced from kinetic studies,[1] the equilibrium between the nitro and aci forms appears to be established through the aci ion rather than by direct migration of a proton from the $\alpha$-carbon to the oxygen.

The *concentration* ionization constant of the nitro form, $K_N$, may be defined by the equation

$$K_N = [\text{Aci}^-][H_3O^+]/[\text{Nitro}] \quad (2)$$

where the brackets are taken to denote concentrations in moles per liter. In turn, the ionization constant of the aci form, $K_{\text{aci}}$, is given by the equation

$$K_{\text{aci}} = [\text{Aci}^-][H_3O^+]/[\text{H Aci}] \quad (3)$$

On division of (3) by (2) the tautomeric equilibrium constant, $K_T$, between the two forms follows as

$$K_T = [\text{H Aci}]/[\text{Nitro}] = K_N/K_{\text{aci}} \quad (4)$$

Junell[2] determined the "apparent" ionization

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(1) Maron and LaMer, *Ann. New York Acad. Sciences*, Vol. XXXIX, 355 (1940).

(2) Junell, Dissertation, Upsala, Sweden, 1935.

constants of nitromethane and nitroethane at 0° by measuring with a hydrogen electrode the *p*H of solutions of these substances in presence of high concentrations of borates or phosphates as buffers. He thus obtained what he called the "apparent" ionization constants, $K'$, defined as

$$K' = [\text{Aci}^-][\text{H}_3\text{O}^+]/[\text{H Aci} + \text{Nitro}] \qquad (5)$$

However, since it was shown by Maron and LaMer[3] and confirmed in this investigation, that the amount of aci form present at equilibrium is negligibly small compared to the concentration of the nitro form, the $K$'s of Junell must be essentially identical with $K_N$. For nitromethane Junell found $K_N = 2.6 \times 10^{-11}$, while for nitroethane $K_N = 2.7 \times 10^{-9}$. The average deviations from the mean amounted to approximately ±10% for nitromethane and ±8% for nitroethane. These appear to be the only available measurements on $K_N$ of nitroparaffins, although fragmentary data of Junell on nitroisopropane tend to indicate that the nitro constant for this substance is considerably larger than that for nitroethane.

The only available information on the ionization constants of the aci nitroparaffins are $K_{\text{aci}} = 6 \times 10^{-4}$ for nitromethane and $K_{\text{aci}} = 7 \times 10^{-5}$ for nitroethane at 0° due to Junell, and $K_{\text{aci}} = 4.09 \times 10^{-5}$ for nitroethane at 23° reported by Maron and Shedlovsky.[4]

In view of the interest in the effect of substitutions on the kinetics of prototropic isomerizations and its relation to the ionization constants of the substrate, it was decided to determine the nitro ionization constants of several nitroparaffins at a number of temperatures. At the same time several aci constants were also measured in order to arrive at the tautomeric equilibria. These data are also of interest *per se* for the light they may throw on the influence of substitution on the constants themselves. In this paper are presented data on the nitro constants of nitromethane, nitroethane, and nitroisopropane, on the aci constants of nitroethane and nitroisopropane, and on the tautomeric equilibrium constants of the last two.

## Experimental

(a) **Chemicals and Apparatus.**—The nitromethane and nitroethane used were Eastman Kodak Co. products which were carefully purified by fractional distillation. For nitromethane the fraction boiling at 100.7–101.0° at 748.0 mm. was retained, while for nitroethane the fraction boiling at 112.8–113.0° at 740.5 mm. To eliminate any oxides of nitrogen the distillates were treated first with urea, then with anhydrous sodium sulfate to remove traces of water, and finally were separated from the solids by low temperature molecular distillation.

The nitroisopropane, furnished by Commercial Solvents Corporation, was purified by repeated fractional distillation in a Widmer column. Only the fraction boiling at 119.8° (corrected) was retained. This distillate was also treated with urea, sodium sulfate and redistilled as described above.

All solutions were made up in doubly distilled water. The water still as well as all containers used were of Pyrex glass.

The nitro constants, $K_N$, were determined by measuring the e. m. f.'s of the cells of the type

| | | | |
|---|---|---|---|
| Glass electrode | Nitroparaffin<br>Na Aci | Saturated calomel electrode | (6) |

where the electrolyte consisted of aqueous solutions of the nitroparaffins partially neutralized with sodium hydroxide. The e. m. f.'s were determined with a precision vacuum tube potentiometer utilizing a 6C6 tube as a detector–amplifier, and a 6E5 electron-ray tube as an indicator. The entire measuring circuit as well as the cell assembly was shielded by enclosure in a grounded metal box. The vacuum tube potentiometer was checked against a Leeds and Northrup type K potentiometer, and was found to reproduce the potentials correctly within ±0.1 mv. over the entire range of the instrument, 0–1.5 volts.

The glass electrodes were of the Beckman permanently sealed, shielded type. For solutions of *p*H 8.5 or lower the ordinary electrodes were employed (No. 1190), while for *p*H above 8.5 electrodes of the high *p*H type (No. 1190-E) were used. In all instances the saturated calomel electrode reference was a stick form Beckman electrode No. 1170. The cell consisted of an electrolytic beaker fitted with a rubber stopper, through which the electrodes were inserted. The temperature was maintained constant to ±0.1° by manual regulation of a water-bath contained in a large Dewar vessel. Cell and bath were completely shielded by enclosure in a grounded metal box, and shielded leads were run from the cell to the potentiometer.

(b) **Procedure.**—The glass electrode was standardized before each determination with 0.0500 molar potassium acid phthalate. In case of the high *p*H electrode standardizations were made also with a borate buffer of *p*H 8.945. Both of these buffers were found to give identical results within the experimental error. For the *p*H of the phthalate buffer were taken the values determined by MacInnes, Belcher and Shedlovsky[5] within 0.005 *p*H unit between 12 and 38°. From these standardizations and the measured e. m. f.'s, the *p*H's of the various samples could be calculated readily.

In measuring $K_N$ for nitromethane a definite amount of a standard solution of this substance (0.005–0.017 molar) was placed in the cell and titrated with standard sodium hydroxide solution (*ca.* 0.1 *N*) delivered in 0.25-ml. increments from a calibrated 0.50-ml. tuberculin type hypodermic syringe. The e. m. f. was measured after each increment of base. Since the *p*H values during the course of the titration ranged from about 8.8 to 10.0, the type E

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(3) Maron and LaMer, THIS JOURNAL, **61**, 2018 (1939).

(4) Maron and Shedlovsky, *ibid.*, **61**, 753 (1939).

(5) MacInnes, Belcher and Shedlovsky, *ibid.*, **60**, 1098 (1938).

electrode was used. Equilibrium was established very rapidly, within a minute or less even at the lowest temperature employed, 10°.

To measure $K_N$ for nitroethane standard solutions of the aci sodium salt (0.003–0.007 molar) were prepared, placed in the cell, and then various small quantities of standard nitroethane solution (0.045–0.075 molar) were added progressively from a 2.00-ml. calibrated tuberculin type syringe. It was found that about five minutes were required for the establishment of equilibrium after each addition. At the end of this time the e. m. f.'s were steady and reproducible.

In the case of nitroisopropane $K_N$ was determined by measuring the $p$H's of solutions made up by the addition of standard sodium hydroxide to a measured excess of standard nitroisopropane in water (0.05–0.06 molar). Final e. m. f. readings had to be taken twelve to twenty-four hours after each sample was made up, since equilibrium is established here very slowly.

To arrive at the aci constants standard solutions of the sodium aci salts (0.003–0.006 molar) were placed in the cell and allowed to come to equilibrium with the thermostat. Measured quantities of standard hydrochloric acid, corresponding to 40–80% of the amount necessary to convert the aci salt to the acid, were then quickly added from a syringe, and the time recorded. Due to the isomerization of the liberated acid, the e. m. f. was found to drift with time. However, within the experimental uncertainty the variation of e. m. f. with time was linear, and hence the e. m. f.'s observed at various times could be plotted against the time and extrapolated back to yield the initial $p$H. This procedure gave concordant results for the $p$H and satisfactory constants for $K_{aci}$.

In all $K_N$ calculations the aci-ion and nitroparaffin concentrations were deduced from the amounts of standard base and nitroparaffin solutions used, due corrections being made for the hydrolysis of the aci salt. Again, in determining the aci constants the aci acid concentration was taken as equal to the hydrochloric acid added less the amount dissociated as obtained from the $p$H. This procedure is justified by Junell's[2] bromination titrations which show that on addition of mineral acids to aci salts the *initial* product is entirely the aci acid.

During the $K_N$ and $K_{aci}$ measurements on nitroisopropane it was observed that reproducible results could not be obtained when the solution of the aci salt was made up in a separate vessel and then transferred to the cells. Moreover, when this was done the e. m. f. values changed irreversibly by as much as 0.01–0.02 volt on shaking the cell. However, when the solution was prepared directly *in the cell*, reproducible potentials could be obtained which did not change perceptibly on shaking. In view of this behavior all nitroisopropane solutions were made up directly in the cells. Further, it was found necessary to make all measurements on sodium nitroisopropane solutions within twelve to twenty-four hours after preparation, as apparently the solutions are not very stable and show after twenty-four hours sufficient decomposition to affect the results.

## Results

In Table I are shown data obtained in the course of a single titration of nitromethane with sodium hydroxide at 25°, and the values of $pK_N$ calculated therefrom. These data are typical of all the $K_N$ measurements reported here. In the case of nitromethane it was not possible to obtain reproducible results for $K_N$ when the $p$H of the solution rose above ten. Above this value the $p$H readings drifted constantly toward lower values and the solution became colored on standing, indicating thus decomposition. However, between $p$H 8.5–10 no significant drifts in $p$H or coloring of the solution were observed.

TABLE I

TYPICAL DATA FOR DETERMINATION OF $K_N$ FOR NITROMETHANE AT 25°

40.00 ml. $CH_3NO_2$ (0.01788 $N$) titrated with 0.1242 $N$ NaOH.

| NaOH, ml. | $p$H | [Nitro] | [Aci] | $pK_N$ |
|---|---|---|---|---|
| 0.252 | 8.871 | 0.01699 | 0.00077 | 10.215 |
| .504 | 9.201 | .01612 | .00153 | 10.224 |
| .756 | 9.391 | .01528 | .00227 | 10.219 |
| 1.008 | 9.521 | .01442 | .00301 | 10.201 |
| 1.260 | 9.645 | .01359 | .00374 | 10.205 |
| 1.512 | 9.746 | .01276 | .00446 | 10.203 |

As data typical of the $K_{aci}$ measurements may be taken those shown in Table II for nitroethane at 25°. Finally, in Table III is given a condensed summary of all the results obtained in this investigation for $K_N$ of nitromethane, nitroethane, and nitroisopropane, at three temperatures in each instance, while in Table IV is given a summary of the results for $K_{aci}$ of nitroethane and nitroisopropane. In the case of nitromethane the isomerization of the aci form to the nitro on addition

TABLE II

DETERMINATION OF $K_{aci}$ FOR NITROETHANE AT 25°

| [Aci] | [H Aci] | $p$H | $pK_{aci}$ |
|---|---|---|---|
| 0.000632 | 0.00236 | 3.834 | 4.408 |
| .000961 | .00229 | 4.029 | 4.406 |
| .001420 | .00447 | 3.899 | 4.398 |
| .001788 | .00364 | 4.101 | 4.410 |

TABLE III

CONDENSED SUMMARY OF RESULTS FOR $K_N$

| $t$, °C. | No. of detns. | $pK_N$ | Max. dev. $pK_N$ | $K_N$ |
|---|---|---|---|---|
| | | Nitromethane | | |
| 10.0 | 15 | 10.450 ± 0.008 | −0.019 | 3.55 ± 0.07 × $10^{-11}$ |
| 18.0 | 19 | 10.332 ± .008 | − .029 | 4.66 ± .09 × $10^{-11}$ |
| 25.0 | 16 | 10.211 ± .009 | − .020 | 6.15 ± .12 × $10^{-11}$ |
| | | Nitroethane | | |
| 18.0 | 4 | 8.490 ± 0.004 | +0.007 | 3.24 ± 0.03 × $10^{-9}$ |
| 25.0 | 14 | 8.456 ± .008 | − .014 | 3.50 ± .06 × $10^{-9}$ |
| 30.0 | 5 | 8.442 ± .003 | − .005 | 3.61 ± .02 × $10^{-9}$ |
| | | Nitroisopropane | | |
| 25.0 | 4 | 7.675 ± 0.034 | −0.040 | 2.12 ± 0.15 × $10^{-8}$ |
| 30.0 | 3 | 7.634 ± .009 | ± .013 | 2.32 ± .05 × $10^{-8}$ |

TABLE IV

CONDENSED SUMMARY OF RESULTS FOR $K_{aci}$ AND $K_T$

| $t$, °C. | No. of detns. | $pK_{aci}$ | Max. dev. $pK_{aci}$ | $K_{aci}$ | $K_T = K_N/K_{aci}$ |
|---|---|---|---|---|---|
| | | | Nitromethane | | |
| 25.0 | .. | ........... | ..... | ................. | $1.1 \times 10^{-7}$[a] |
| | | | Nitroethane | | |
| 18.0 | 3 | $4.424 \pm 0.001$ | $+0.003$ | $3.77 \pm 0.01 \times 10^{-5}$ | $8.44 \times 10^{-5}$ |
| 25.0 | 4 | $4.406 \pm .004$ | $-.008$ | $3.93 \pm .04 \times 10^{-5}$ | $8.91 \times 10^{-5}$ |
| 30.0 | 4 | $4.407 \pm .007$ | $-.014$ | $3.92 \pm .07 \times 10^{-5}$ | $9.21 \times 10^{-5}$ |
| | | | Nitroisopropane | | |
| 25.0 | 4 | $5.112 \pm 0.003$ | $-0.006$ | $7.73 \pm 0.06 \times 10^{-6}$ | $2.75 \times 10^{-3}$ |
| 30.0 | 5 | $5.107 \pm .008$ | $+.015$ | $7.82 \pm .15 \times 10^{-6}$ | $2.97 \times 10^{-3}$ |
| 35.0 | 4 | $5.121 \pm .004$ | $-.008$ | $7.57 \pm .007 \times 10^{-6}$ | .......... |

[a] Calculated from $K_{aci}$ estimated at 0° by Junell.[2]

of a strong acid is too rapid to permit determination of $K_{aci}$ with any reliability. Accompanying the average values of $p$K found are the average and maximum deviations observed from the mean, and the values of $K_N$ corresponding to $pK$. Moreover, in the last column of Table IV are tabulated the tautomeric equilibrium constants, $K_T$, calculated from $K_N$ and $K_{aci}$ by means of equation (4).

It should be remarked that all these results were calculated on the assumption that the $p$H observed was a measure of the hydrogen ion *concentration*, and that no corrections were introduced for variation of the ionic strength. However, these assumptions should introduce no significant error, since in all cases the ionic strength was low, being usually 0.004 and never exceeding 0.007. In fact, the corrections from such low ionic strengths are of the same order of magnitude as the uncertainties of the measurements, and may thus be neglected. The ionic strengths used in this work are in all instances very much lower than those employed by Junell[2] or by Maron and Shedlovsky.[4]

The significant factors affecting the over-all accuracy of the $K_N$ values are the uncertainties in the measured potentials and the volumes of reagents delivered from the syringes. Since the e. m. f.'s on any given sample were reproducible to ±0.2 mv., the uncertainty in the $p$H measurements amounts to about ±0.007 unit. Adding to this 0.005 $p$H unit uncertainty in the value of the phthalate buffer employed, the total possible error in the observed $p$H's may be as high as ±0.012 unit. Further, as the uncertainty in the addition of the small quantities of reagents amounted to about ±1.0–1.5%, the over-all accuracy of the $K_N$ values may be considered to be within ±0.018 $pK$ unit.

This is certainly the maximum possible uncertainty in the $pK_N$ values of nitromethane and nitroethane. Due to the long periods of time required to reach equilibrium in the case of nitroisopropane, and due to the fact that solutions of this substance behave essentially as an unbuffered system, the error in the $K_N$ values for nitroisopropane may be somewhat greater. It is of interest to observe here that several determinations of $K_N$ colorimetrically using brom thymol blue gave results in agreement with the potentiometric method within the precision of the former.

The over-all accuracy of the $K_{aci}$ constants is not quite as high as that of the $K_N$'s. In these experiments the total uncertainty in the $p$H may have amounted to as much as ±0.017 unit, while the uncertainty in the reagent concentrations to 0.008–0.013 $pK$ unit. The accuracy of $pK_{aci}$ should be, therefore, within ±0.025–0.030 unit.

In Table V are tabulated certain thermodynamic quantities deducible from the data given in Tables III and IV. The second column gives the free energies of ionization, $\Delta F_i^0$, at 25° for the various aci and nitroparaffins, while the third column gives the heats of ionization, $\Delta H_i$ for the nitro forms obtained from plots of $pK_N$ *vs.* $1/T$ shown in Fig. 1 (A and B). These plots are seen to be linear within the experimental error. Since the aci constants appear to be essentially independent of temperature in the range investigated, no attempt was made to evaluate heats of ionization for these. Finally, in the fourth column are given the standard free energy changes on tautomerization, $\Delta F_T^0$, while in the last column the heats of these changes, $\Delta H_T$. $\Delta H_T$ for nitro-

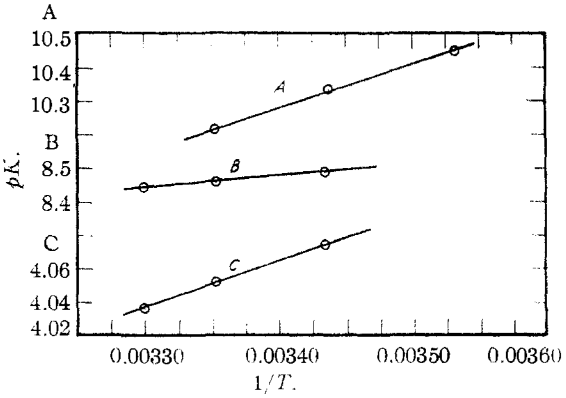

Fig. 1.—Plot of $pK$ vs. $1/T$: A, $pK_N$ for nitromethane; B, $pK_N$ for nitroethane; C, $pK_T$ for nitroisopropane.

ethane was determined from the plot of $pK_T$ vs. $1/T$ shown in Fig. 1 (C), while that for nitroisopropane was calculated from the two available points. In view of this $\Delta H_i$ and $\Delta H_T$ for nitroisopropane are believed to be less accurate than the other $\Delta H$ values.

TABLE V

THERMODYNAMIC DATA FOR IONIZATION AND ISOMERIZATION AT 25° (IN CALORIES/MOLE)

| Substance | $\Delta F_i^0$ | $\Delta H_i$ | $\Delta F_T$ | $\Delta H_T$ |
|---|---|---|---|---|
| Nitromethane | 13,930 | 6220 | 9500 | .. |
| Nitroethane | 11,530 | 1710 | 5520 | 1280 |
| Nitroisopropane | 10,470 | 3400 | 3500 | 2800 |
| Aci-nitroethane | 6,010 | .. | .. | .. |
| Aci-nitroisopropane | 6,970 | .. | .. | .. |

## Discussion

Extrapolation of the log $K_N$ vs. $1/T$ plot for nitromethane to 0° gives $K_N = 2.33 \times 10^{-11}$, which compares favorably with Junell's $K_N = 2.6 \times 10^{-11}$ considering the uncertainty in the latter value. For nitroethane extrapolation of a similar plot to 0° yields $K_N = 2.67 \times 10^{-9}$, which is in excellent accord with Junell's $K_N = 2.7 \times 10^{-9}$. The value of $K_{aci} = 3.93 \times 10^{-5}$ for nitroethane at 25° is, in turn, in good agreement with the value $K_{aci} = 4.09 \times 10^{-5}$ at 23° reported by Maron and Shedlovsky.[4] The latter result was obtained at ionic strengths higher than those employed here, and a correction for these would bring the two values even closer together.

Comparison of the nitro dissociation constants at 25° reveals that substitution of a methyl group for an $\alpha$-hydrogen in nitromethane increases the ionization constant by a factor of about 57, while substitution of a second methyl group increases the constant still further by a factor of six. This effect of substitution on the dissociation constants of the nitro compounds is in marked contrast to its effect on the *rate* of prototropic isomerization, which decreases with the replacement of hydrogens by methyl groups.[6] Again, the observed effect of substitution on the nitro ionization constants is hardly that to be anticipated on the basis of inductive effects due to methyl groups, as these groups are considered to be electron repulsive and should lead, therefore, to a firmer binding of the protons to the $\alpha$-carbon.

Utilizing the ionization constant of aci-nitromethane suggested by Junell and assuming it to be independent of temperature, we observe that the substitution of one methyl group in aci nitromethane lowers $K_{aci}$ by a factor of about fifteen, while substitution of a second methyl group lowers the constant further by a factor of about five. The effect of methyl substitution here is thus in the same direction as that observed in the substitution of methyl groups in the $\alpha$-position in carboxylic acids, except that the effect with the aci acids is much more marked, involving a factor of about five in passing from aci nitroethane to aci nitroisopropane, whereas substitution of a methyl group in acetic acid to yield iso-propionic acid lowers the ionization constant by only a factor of 1.4. In general, however, substitution shifts the aci constants in the direction which would be predicted on the basis of the inductive effect of methyl groups as contrasted with that of hydrogen atoms.

The results indicate that the ionization constants of the aci acids are essentially independent of the temperature in the range 18-35°. Although the precision of the measurements is not sufficiently high to establish definitely whether the constants pass through a maximum analogous to the carboxylic acids, nevertheless, the trend of the data indicates that this may be the case.

From the values of the tautomeric equilibrium constants, $K_T$, it is apparent that methyl substitution greatly increases the stability of the aci form with respect to the nitro in aqueous solutions. Thus substitution of one methyl group increases $K_T$ by a factor of 90, while a second methyl group increases the constant still further by a factor of about 30. The tautomerism between aci and nitroparaffins is analogous to the tautomerism between keto and enol forms in carbonyl compounds. However, whereas Conant and Thompson[7] found that in an inert solvent or in the vapor

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(6) Maron and LaMer, THIS JOURNAL, **60**, 2588 (1938).

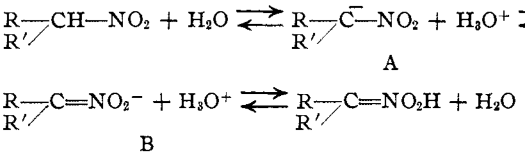
(7) Conant and Thompson, *ibid.*, **54**, 4044 (1932).

phase substitution of alkyl groups on the α-carbon of a carbonyl compound shifted the equilibrium in favor of the keto form, substitution in the case of the nitroparaffins is again in marked contrast and favors the aci form. It seems very questionable that this effect of substitution can be accounted for by solvent effects alone.

It should also be observed that temperature increase favors the aci form in aqueous solution, as is evidenced by the results on $K_T$ of nitroethane and nitroisopropane.

From the standpoint of the Brönsted theory of general base catalysis and the relation of the catalytic constants to the basic strength of the catalyst, the above described and generally accepted behavior of the nitroparaffins presents another difficulty. If the aci and nitro acids ionize to yield the same anions, then when such anions are used as bases what is the basic constant, $1/K_N$ or $1/K_{aci}$? Obviously it cannot be both, nor can it be decided *a priori* whether it will be one or the other. As a matter of fact, in view of the difficulties and anomalies pointed out, it is questionable whether the formulation of the nitroparaffin equilibria, as expressed in equation (1), is correct.

The unusual effect of substitution on the nitro constants can be explained, and the base strength dilemma of the anions of the nitro and aci acids can be resolved if we postulate that the anions of the nitroparaffin acids exist not in one form, $\begin{matrix}R\\R'\end{matrix}\!\!>C{=}NO_2^-$, but in two tautomeric forms in equilibrium, $\begin{matrix}R\\R'\end{matrix}\!\!>C^-{-}NO_2$ and $\begin{matrix}R\\R'\end{matrix}\!\!>C{=}NO_2^-$; *i. e.*, that the equilibrium between the aci and nitro forms is not established according to equation (1), but according to



$$\begin{matrix}R\\R'\end{matrix}\!\!>CH{-}NO_2 + H_2O \rightleftharpoons \underset{A}{\begin{matrix}R\\R'\end{matrix}\!\!>\bar{C}{-}NO_2} + H_3O^+ \rightleftharpoons$$
$$\underset{B}{\begin{matrix}R\\R'\end{matrix}\!\!>C{=}NO_2^-} + H_3O^+ \rightleftharpoons \begin{matrix}R\\R'\end{matrix}\!\!>C{=}NO_2H + H_2O \qquad (7)$$

This suggestion is in accord with the kinetic evidence[1] that the carbanion A is the first product of the removal of a proton in the neutralization of a nitroparaffin. Shriner and Young[8] attributed the optical activity shown by the sodium salt of 2-nitro-octane in alcoholic solution at low temperatures to the presence of a solvated carbanion formed from A. Hammett[9] proposes that the aci ion is a resonance hybrid of the A and B forms. If the A form does not pass over completely into the B form, there is evidently some of it present in solution along with B, and the concentrations of aci ions used in the evaluation of $K_N$ and $K_{aci}$ in the present investigation must obviously be the sums of the concentrations of A and B.

In terms of the formulation given in (7) we may define the primary dissociation constant of the nitro form, $K'_N$, as

$$K'_N = [H_3O^+][A]/[\text{Nitro}] \qquad (8)$$

that of the aci form, $K'_{aci}$, as

$$K'_{aci} = [H_3O^+][B]/[\text{H Aci}] \qquad (9)$$

and the equilibrium ratio of B to A as

$$K = [B]/[A] \qquad (10)$$

Insertion of these new definitions into equations (2), (3) and (4) readily reveals that

$$K_N = K'_N(K + 1) \qquad (11)$$
$$K_{aci} = K'_{aci}((K + 1)/K) \qquad (12)$$

and

$$K_T = K_N/K_{aci} = (K'_N/K'_{aci})K = K'_TK \qquad (13)$$

where $K'_T = K'_N/K'_{aci}$. From these equations it is apparent that $K_N$ and $K_{aci}$ as given in this paper are not the direct ionization constants, but are related to these through the constant $K$. Further, it follows from this formulation that the basic constants of A and B are different, and that in any base catalyzed reaction in which these may be used the behavior anticipated is to be not that of a single catalytic anion, but of a mixture of two anions of different basic strengths.

Before the effect of substitution on $K_N$ can be explained some decision with respect to the magnitude of $K$ is necessary. All indications are that $K$ is large. First, because of the presence of the electron on the carbon rather than on oxygen, as in B, the anion A can hardly be expected to be very stable with respect to B. Again, in all probability the anion B exists in two resonating structures which would further enhance its stability. Both of these factors, therefore, point to a much larger concentration of B over A in solution at equilibrium, and hence a large value of $K$.

If $K$ is large, then equations (11) and (12) reduce essentially to $K_N = (K'_NK)$ and $K_{aci} = K'_{aci}$. In the latter instance the effect of substitution of methyl groups for hydrogen should lead to a more or less normal decrease in $K_{aci}$ with substitution, and such is actually the case. With $K_N$, however, two inductive effects of substitution must be consid-

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(8) Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

(9) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 67.

ered, that on $K'_N$ and on $K$. As far as $K'_N$ is concerned, the firmer attachment of protons to the $\alpha$-carbon may be expected to result again in a decrease in $K'_N$ on passing from nitromethane to nitroethane to nitroisopropane. On the other hand, the stronger affinity for protons resulting from replacement of hydrogens with methyl groups is equivalent to a decrease in electron affinity of the carbon, and hence substitution should favor form B over A with a resultant increase in $K$. As the increase in $K$ may well outweigh the decrease in $K'_N$, $K_N$ may increase appreciably with substitution, as has been observed here. This explanation would account also for the large increase in the tautomeric equilibrium constants $K_T$ observed here on going from nitromethane through nitroethane to the isopropane.

## Summary

1. Nitro ionization constants have been determined for nitromethane, nitroethane and nitroisopropane, and aci ionization constants for nitroethane and nitroisopropane at several temperatures.

2. From these constants have been calculated the nitro–aci tautomeric constants for nitromethane, nitroethane and nitroisopropane.

3. Values of $\Delta F^0$ and $\Delta H$ for ionization and tautomerization as ascertained from these data are given.

4. The effect of substitution on the constants is discussed. It is shown that assumption of a common anion for the nitro and aci forms leads to inconsistencies in the influence of substitution on the nitro constants, and yields an anion with two basic strengths.

5. An alternate formulation of the nitro-aci relations in the nitroparaffins is presented which resolves these anomalies.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

# The Thermodynamics of Aqueous Solutions of Sodium Chloride at Temperatures from 15–45° from e. m. f. Measurements on Cells with Transference

BY G. J. JANZ[1] AND A. R. GORDON

The investigation described here of the electromotive force of the cell with transference

$$\text{Ag, AgCl/NaCl}(m_1)//\text{NaCl}(m_2)/\text{AgCl, Ag}$$

at temperatures from 15 to 45° was undertaken as a natural complement to that recently reported[2] from this Laboratory giving the corresponding data for potassium chloride solutions. Brown and MacInnes[3] in their classic investigation of this cell were restricted to measurements at 25°, but since transference numbers[4] are now available for the whole temperature range, it is now possible to compare the results of the e. m. f. measurements with the thermal data; fortunately, for sodium chloride solutions the latter are unusually complete. Finally, the accompanying paper[5] gives the results of an isopiestic comparison of sodium and potassium chloride solutions at concentrations less than tenth molal and thus provides an additional independent check on the accuracy of all the measurements.

## Experimental

The cell, the electrodes and general experimental technique were the same as in the measurements with potassium chloride; the true reversible e. m. f. was determined both by the electrode reversal procedure of Brown and MacInnes and by static bias potential measurements before and after a run with both electrodes in the same solution (see ref. 2).

The sodium chloride was British Drug Houses Analar, twice recrystallized from conductivity water. The solutions were made up gravimetrically from the salt, which had been fused in platinum in an atmosphere of dry carbon dioxide-free nitrogen, and conductivity water (specific conductance 1.0–1.2 × $10^{-6}$); after preparation, the solutions were swept out, immediately before being forced into the cell, with carbon dioxide-free air which after going through the potassium hydroxide bubblers had passed through a further bubbler containing conductivity water. In cal-

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[1] Canadian Industries Limited Fellow in Chemistry.

[2] W. J. Hornibrook, G. J. Janz and A. R. Gordon, THIS JOURNAL, **64**, 513 (1942).

[3] A. S. Brown and D. A. MacInnes, *ibid.*, **57**, 1356 (1935).

[4] R. W. Allgood and A. R. Gordon, *J. Chem. Phys.*, **10**, 124 (1942).

[5] A. R. Gordon, THIS JOURNAL, **65**, 221 (1943).