Sample	1	2	3	4	5	Mean
H	15600	14200	14850	14600	15400	15000 ± 475

The average deviation from the mean was therefore about ±3%; the square root of the sum of the squared deviations ±3.5%. The physical constants of the monomers and the heats of polymerization are given.

Substance	Styrene	Methyl metha-crylate	Vinyl acetate
B. p., °C.	145–6	100	73
d^{20}_4	0.908	0.937	0.934
n^{20}_D	1.543	1.414	1.396
Ext. of polymerization in %	35–85	98–99	95
Temp. in °C.	70–140	60–90	80
Time, hours	$^1/_2$–2	$^1/_2$	$^1/_2$
H (mean), cal./mol.	15000	7900	8000
Av. dev. fr. mean	±470	±400	±400

It is a pleasant duty for the authors to express their sincerest appreciation to Mr. Dan Whyte, President of the Jay Novelty Company of New York City, whose interest in the subject enabled us to build the described calorimeter and to carry out the measurements.

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Acid Strengths of Aliphatic Nitro Compounds

BY G. W. WHELAND AND JOHN FARR

Turnbull and Maron[1] have recently reported the measurement of the aci dissociation constants of both the nitro and the aci forms of several aliphatic nitro compounds. We had previously been making these same measurements by the same experimental method. Our provisional values of the *pK*'s of the nitro forms at 25° are: nitromethane, 10.24; nitroethane, 8.60; 1-nitropropane, 8.98; and 2-nitropropane, 7.7–7.8. All values are corrected for salt-effect and for hydrolysis, and have probable errors of ±0.04 as judged by the internal consistency of the data. These figures are mostly in satisfactory agreement with those of Turnbull and Maron, but the discrepancy for nitroethane is somewhat larger than the probable error in either set of measurements. Under the circumstances, we have discontinued work on the problem.

The *pK*'s of the nitro forms decrease in the unexpected order: nitromethane > nitroethane > 2-nitropropane. The opposite order might have been anticipated, since methyl groups ordinarily decrease acid strengths. Turnbull and Maron have advanced an explanation of this fact on the assumption that the ions of the nitro and aci forms are different, and are not identical with each other as they would have to be if resonance occurs between the two corresponding structures. Since this assumption seems to us to be rather improbable, we wish to call attention here to the following alternative explanation, which we consider to rest upon a more satisfactory theoretical basis. The ionizable proton in 2-nitropropane, for example, is extremely close both to the nitro group and to the methyl groups in question. Consequently, the lines of force between the large dipole moments of the nitro group and the proton must pass largely through the methyl groups—that is, through a region of relatively low dielectric constant. As a result, the electrostatic interaction, which is responsible in the main for the measurable acidities of the substances, must be greater for 2-nitropropane than for nitromethane, in which the corresponding lines of force pass largely through the solvent of high dielectric constant. Nitroethane is of intermediate acidity, as could have been predicted. The fact that the expected order of increasing *pK*'s (nitromethane < nitroethane < 2-nitropropane) is observed in the aci forms can be related to the fact that in these aci forms the ionizable protons are farther removed from the nitro and methyl groups, so that the lines of force pass largely through the solvent in all cases. Consequently, the usual direct effects of the methyl groups in decreasing acid strengths have a chance to operate, as in the analogous carboxylic acids. Furthermore, in 1-nitropropane, the terminal methyl group is farther removed from the proton, and so it it exerts only its direct effect in making the substance less acidic than nitroethane. It is not clear to us how the explanation of Turnbull and Maron would apply to this substance.

The foregoing discussion is based upon a closely similar one given by Westheimer and Shookhoff[2] in regard to the acid constants of substituted malonic acids.

We wish to thank the Commercial Solvents Corporation for furnishing the 1-nitropropane and 2-nitropropane used in our work.

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[1] D. Turnbull and S. H. Maron, THIS JOURNAL, **65**, 212 (1943).

[2] F. H. Westheimer and M. W. Shookhoff, *ibid.*, **61**, 555 (1939).