

at diminished pressure giving 46.2 g. (84%) of colorless liquid, b. p. 135–138° (18 mm.), n_D^{20} 1.5344.

An alcoholic solution of the product gave a deep blue-green color with ferric chloride. The α -naphthylurethan of 6-allylcreosol was prepared in 70% yield; after one recrystallization from ligroin it melted at 132–132.5°.

Anal. Calcd. for $C_{22}H_{21}O_3N$: C, 76.1; H, 6.1. Found: C, 76.1; H, 6.3.

3,4-Dimethoxy-5-allyltoluene (V).—To 130 cc. of 2 *N* sodium hydroxide solution in a glass-stoppered bottle was added 46.2 g. (0.26 mole) of 6-allylcreosol (IV) and one-third of a portion of 32.8 g. (0.26 mole) of dimethyl sulfate; the mixture was shaken vigorously at intervals for five minutes, after which another third of the dimethyl sulfate was added; the final addition was made after a similar period. An oily layer separated and was extracted with ether. The ether extract was washed twice with water and dried over calcium chloride. After removal of the ether, distillation at diminished pressure gave 43.0 g. (86%) of colorless liquid, b. p. 125–135° (12 mm.), n_D^{20} 1.5240.

2,3-Dimethoxy-5-methylbenzoic Acid (IX).—Two grams of 3,4-dimethoxy-5-allyltoluene was treated with aqueous permanganate as described above in the preparation of 2-methoxy-4-methylphenoxyacetic acid. The product was crystallized from petroleum ether (b. p. 60–70°) containing a little benzene; yield, 0.1 g. of white crystals, m. p. 91.5–92.5°. The product dissolved with effervescence in 5% sodium bicarbonate solution.

This compound was also obtained in 20–30% yield by the oxidation of 3,4-dimethoxy-5-propenyltoluene (VI).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 61.4; H, 6.3.

6-Propenylcreosol (VII).—Ten grams of potassium hydroxide pellets was dissolved in 100 cc. of diethylene glycol by heating to 160° in an oil-bath; to the hot solution was added 17.5 g. (0.1 mole) of 6-allylcreosol (IV). Heating (150–170°) was continued for one hour. When cool, the mixture was poured into 200 cc. of water and acidified with hydrochloric acid. The brown oily layer was extracted with petroleum ether (b. p. 60–70°), the solvent evaporated, and the residue distilled through a Widmer column. The boiling point rose gradually, and no clean-cut fractions appeared; a total of 10.5 g. of liquid, b. p. 86–120° (1 mm.), was collected. The residue from the distillation (3.5 g.) solidified upon cooling, and extraction with petroleum ether gave 1.9 g. of light tan crystals, m. p. 60–62°. The crude material was dissolved in dilute alkali, treated with Norit, and precipitated with dilute hydrochloric acid; the purified product, m. p. 61–62°, was still not white.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.1; H, 8.0.

3,4-Dimethoxy-5-propenyltoluene (VI).—Twenty grams of potassium hydroxide pellets was dissolved in 200 cc. of diethylene glycol by heating and stirring. When the temperature of the solution had reached 165° water began to boil off; after most of this had been removed, 41.0 g. (0.213 mole) of 3,4-dimethoxy-5-allyltoluene (V) was added. For the next twenty minutes the solution was stirred and the temperature maintained at 175–185°. After cooling to 120° the dark red liquid was poured into

400 cc. of cold water, whereupon an oily layer separated. The latter was extracted with petroleum ether (b. p. 60–70°) and the ether solution dried over calcium chloride. After removal of the solvent, distillation at diminished pressure gave 16.1 g. (39%) of colorless liquid, b. p. 109–111° (1 mm.), n_D^{20} 1.5468.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
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The Heat of Polymerization of Some Vinyl Compounds

BY G. GOLDFINGER, D. JOSEFOWITZ AND H. MARK

The heat liberated in polymerization reactions is sometimes considerable and may interfere with the easy control of the process. Moreover, knowledge of the magnitude of the heat evolution may also be of use in connection with kinetic and equilibrium considerations. We have, therefore, undertaken the direct measurement of the heat of polymerization of several important substances.

Luschinsky¹ has already determined the heat of polymerization of styrene from measurements of the heats of combustion of the monomer and the polymer. These measurements can indeed be made with great accuracy, but as these heats may well be 100 times larger than the heat of polymerization, the errors in the latter may be magnified 100-fold. We have, therefore, resorted to the methods of adiabatic calorimetry and have utilized for this purpose a 100-cc. cylindrical Dewar flask submerged in a 1-liter oil-bath whose temperature could be raised uniformly by means of an insulated heater and a rapid stirrer. The flask contained 50 cc. of water in which was submerged an hermetically sealed glass tube containing 8 g. of the monomer. The adiabaticity was controlled to within $\pm 0.25^\circ$ by means of a galvanometer sensitive to 0.05° . The polymerization was initiated by heat. The temperature rise of the liquid in the Dewar flask and hence the heat evolved was measured to 0.25° .

The substances studied were purified by repeated vacuum distillation of commercial materials.

Measurements were made on four or five samples of each substance. The individual molar heats of polymerization (H) obtained with styrene were typical and were as follows, expressed in calories

(1) W. V. Luschinsky, *Z. physik. Chem.*, **A188**, 384 (1938).

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

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

Substance	Styrene	Methyl methacrylate	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	$\frac{1}{2}$ -2	$\frac{1}{2}$	$\frac{1}{2}$
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.

POLYTECHNIC INSTITUTE OF BROOKLYN
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Acid Strengths of Aliphatic Nitro Compounds

BY G. W. WHELAND AND JOHN FARR

Turnbull and Maron¹ 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 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 Shookhoff² 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).