values of the function $\Delta(F^\circ - H^\circ_0)/T$ and values of the true ΔH°_0 corresponding to the several measured values of $\Delta F^\circ/T$. We thus have the following:

$$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g);\ \Delta H^\circ_0 = 13{,}421 \pm 53 \text{ cal. per mole};\ \Delta F^\circ_{298.1} = 3547 \pm 60 \text{ cal. per mole};\ \Delta H^\circ_{298.1} = 13{,}379 \pm 60 \text{ cal. per mole};\ \Delta S^\circ_{298.1} = 32.98 \text{ E. U. (Method III)} \quad (11)$$

The differences between the values of $\Delta F^\circ_{298.1}$ and $\Delta H^\circ_{298.1}$ as given by Methods II and III are partly differences in the averaging of the values of the empirical algebraic ΔH°_0 on the one hand and the true ΔH°_0 on the other, and partly to the use of an average empirical equation for the heat capacity of nitric oxide in Method II. Equation 9 (Method II) is to be used when algebraic equations are required.

Since the completion of this investigation a paper by M. Tzentnershver and T. Checinski[13] dealing with the decomposition of silver nitrite has appeared. These authors investigated the decomposition reaction by a dynamic method. In the temperature range in which equilibrium is established with sufficient rapidity and in which their dynamic method may then be expected to yield equilibrium measurements, their results confirm our own. The reverse or synthesis reaction was not investigated, and hence they failed to observe solid solution effects at the higher temperature.

Summary

The equilibrium between solid silver nitrite, silver and silver nitrate and gaseous nitric oxide has been measured. We have calculated values of the $\Delta(F^\circ - H^\circ_0)/T$ function from existing data and have calculated the standard free energy, heat content and entropy increases at 25° by 3 independent methods.

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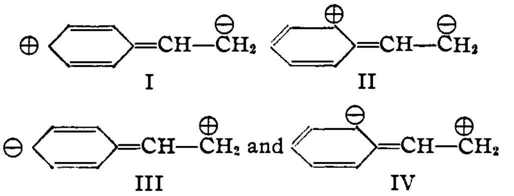
[13] M. Tzentnershver and T. Checinski, *Bull. intern. acad. polonaise sci. Classe sci. math. nat.*, **1935A**, 156 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

The Dipole Moments of Some Styrene Derivatives

BY H. L. GOEBEL AND H. H. WENZKE

It is a characteristic of unsaturated hydrocarbon groupings to attract electrons relatively to an alkyl group. Thus toluene has a moment of 0.4 with the negative end toward the benzene ring. In styrene two unsaturated groupings are linked together. The compound has a moment which experiment has shown to be opposite in direction to that of toluene.[1] In addition to the effect of induction the ethylenic grouping is in resonance with the benzene ring. Some of the more important forms of styrene are



The contributions of I and II are evidently greater than those of III and IV. The relative contributions of these forms are influenced by the replacement of one of the beta hydrogen atoms by other atoms or groups.

Preparation of Compounds.—The dioxane used as the solvent in these determinations was purchased from the Eastman Kodak Company. It was dried by refluxing with sodium and then distilled in all-glass Widmer distilling apparatus.

Cinnamic acid, methyl cinnamate, cinnamyl alcohol, cinnamyl chloride, γ-phenyl-*n*-propyl alcohol and γ-phenyl-*n*-propyl bromide also were purchased from the Eastman Kodak Company. These compounds according to their physical states at room temperature were either crystallized from suitable solvents or distilled through an efficient column so as to check melting points or boiling points reported in the literature.

Cinnamoyl amide was obtained by treating cinnamic anhydride with an ammonia solution according to a method reported by Autenrieth.[2] The amide was crystallized several times from hot water.

β-Cyanostyrene was prepared from cinnamoyl amide and phosphorus pentoxide in a manner similar to that proposed by Moureu and Lazennec[3] for preparing the corresponding acetylenic nitrile from the amide. The compound was crystallized repeatedly from a mixture of petroleum and diethyl ethers.

β-Nitrostyrene and *p*-methyl-β-nitrostyrene were prepared from nitromethane[4] and benzaldehyde and tolalde-

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[1] Otto and Wenzke THIS JOURNAL, **57**, 294 (1935).

[2] Autenrieth, *Ber.*, **34**, 186 (1901).

[3] Moureu and Lazennec, *Bull. soc. chim.*, **35**, 524 (1906).

[4] *Org. Syntheses*, **3**, 85 (1923).

TABLE I

PHYSICAL CONSTANTS OF COMPOUNDS

Compound	B. p., °C.	Mm.	M. p., °C.	n^{25}_D	d^{25}
Cinnamic acid			133		
Methyl cinnamate			35.5–36.0		
Cinnamoyl amide			147.5–148.0		
β-Cyanostyrene	135.0–135.5	13	23.5–24.0	1.60010	1.02440
β-Nitrostyrene			57.5–58.0		
p-Methyl-β-nitrostyrene			103.0–103.5		
Cinnamyl alcohol			33. –33.5		
Cinnamyl chloride	119.5–120	18		1.58065	1.08815
γ-Phenyl-*n*-propyl alcohol	120.0–120.5	12		1.52450	0.99873
γ-Phenyl-*n*-propyl bromide	121. –121.5	20		1.54330	1.30879
γ-Phenyl-*n*-propyl chloride	106. –106.5	22		1.52030	1.04259

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF STYRENE DERIVATIVES

Solvent, dioxane; temp., 25°.

c_2	ϵ	
Nitrostyrene		
0.000000	2.2209	1.02745
.007782	2.4326	.....
.009829	2.4866	.....
.012612	2.5574	.....
.019284	2.7314	1.03202
.022549	2.8075	1.03286
.024609	2.8688	1.03310
p-Methyl-β-nitrostyrene		
0.000000	2.2135	1.02769
.008125	2.4854	1.02957
.009287	2.5255	1.02981
.009313	2.5210	1.02983
.010670	2.5667	1.03002
β-Cyanostyrene		
0.000000	2.2135	1.02769
.008514	2.4291	1.02793
.008674	2.4307	1.02767
.009122	2.4432	1.02800
.011670	2.5019	1.02788
Cinnamic Acid		
0.000000	2.2208	1.02779
.014193	2.2953	1.03048
.027914	2.3621	1.03355
.033136	2.3923	1.03474
.034028	2.3959	1.03476
Methyl Cinnamate		
0.000000	2.2157	1.02777
.016054	2.3075	1.02931
.019913	2.3320	1.02967
.028598	2.3767	1.03036
Cinnamoyl Amide		
0.000000	2.2157	1.02777
.007735	2.3665	1.02943
.008840	2.3871	1.02943
.011555	2.4394	1.03033
.011601	2.4453	1.03043
Cinnamyl Alcohol		
0.00000	2.2125	1.02790
.02354	2.3294	1.02874
.03652	2.3987	1.02910
.04232	2.4269	1.02921
Cinnamyl Chloride		
0.000000	2.2185	1.02805
.013560	2.2967	1.02936
.014014	2.2937	1.02964
.015179	2.3082	1.02971
.019194	2.3256	1.02988
γ-Phenyl-*n*-propyl Alcohol		
0.00000	2.2177	1.02837
.03454	2.3733	1.02867
.04123	2.3913	1.02660
.05356	2.4529	1.02581
γ-Phenyl-*n*-propyl Chloride		
0.00000	2.2177	1.02837
.03448	2.3747	1.02867
.03977	2.4001	1.02860
.05064	2.4522	1.02902
γ-Phenyl-*n*-propyl Bromide		
0.00000	2.2177	1.02837
.02595	2.3427	1.04071
.03454	2.3806	1.04481
.04075	2.4126	1.04761

TABLE III

POLARIZATIONS AND MOMENTS OF STYRENE DERIVATIVES

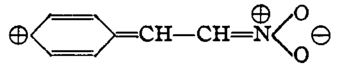
Compound	P_∞	MR_D	$\mu \times 10^{18}$
β-Nitrostyrene	377.2	45.49	4.27
p-Methyl-β-nitrostyrene	470.8	51.55	4.77
β-Cyanostyrene	354.2	43.11	4.14
Cinnamic acid	65.4	45.78	1.78
Methyl cinnamate	76.8	49.31	1.93
Cinnamoyl amide	270.2	48.13	3.61
Cinnamyl alcohol	66.6	39.92	1.79
Cinnamyl chloride	74.8	46.70	1.90
γ-Phenyl-*n*-propyl alcohol	60.7	41.73	1.71
γ-Phenyl-*n*-propyl chloride	64.8	45.09	1.76
γ-Phenyl-*n*-propyl bromide	65.4	47.95	1.78

hyde,[5] respectively. The compounds were crystallized from hot alcohol.

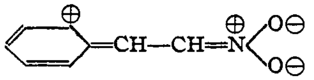
γ-Phenyl-*n*-propyl chloride was prepared from the alcohol by passing dry hydrogen chloride into a mixture of the alcohol and zinc chloride.[6] The product was purified by fractional distillation.

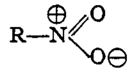
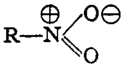
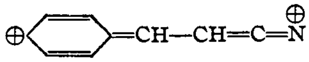
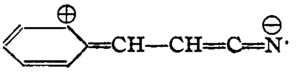
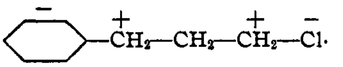
Discussion of Results

The large moment of β-nitrostyrene compared with those of the nitroparaffins is explained readily by the presence of the following electromeric forms in the former compound:



and



In the nitroparaffins the resonance is confined to the nitro group, giving  and  with complete degeneracy within that group so that the two oxygen atoms are attached to the nitrogen atom with equal forces. The moment of nitrobutane is 3.29 while that of β-nitrostyrene is 4.27, almost one unit higher. The moment of *p*-methyl-β-nitrostyrene is 0.5 unit higher than that of β-nitrostyrene. This difference points quite strongly to the fact that the nitro group and the aryl group in both of these compounds are in the *trans* position. β-Cyanostyrene has a moment of 4.14 while that of the corresponding acetylenic compound, phenylpropionitrile, is 4.50. The more important polar structures associated with the β-cyanostyrene are  and  The moment of cinnamoyl amide is 3.61 compared to 3.54 for benzamide. The NH_2 group is very likely frozen in both of these compounds so that rotation about the C—N bond is not possible. The moment of cinnamic acid is 1.78 and is slightly higher than that of acetic acid, which has the value of 1.74 but is lower than that of phenylpropiolic acid. The ionization constants of these compounds follow a similar order. Methyl cinnamate has a higher moment than cinnamic acid. This is consistent with the general relationship between the moments of acids and their esters. The moment of ethyl acetate, for example, is 1.86 which is 0.14 unit higher than that of acetic acid. The moments of γ-phenyl-*n*-propyl bromide and γ-phenyl-*n*-propyl chloride are lower than those of the straight chain saturated halides having several carbon atoms. Thus *n*-butyl chloride and *n*-butyl bromide both have a moment of 2.05[7] while γ-phenyl-*n*-propyl bromide has a moment of 1.78 and γ-phenyl-*n*-propyl chloride has the value 1.76. This is explained readily by an examination of the structure  The moment of toluene has the negative end toward the benzene ring and this moment in part opposes that of the chlorine to carbon moment at the other end of the molecule. The replacement of the two CH_2 groups adjacent to the benzene ring by an ethylenic grouping to form cinnamyl chloride results in an increase in moment. While the inductive influence of the ethylenic grouping will be such as to reduce the moment of chlorine to the carbon atom to which it is attached, the moment of phenylethylene has the positive end toward the benzene ring (opposite to that in toluene). Thus the moment of the aryl part of the molecule in the cinnamyl halide adds to the carbon to halogen moment at the other end of the molecule.

Summary

The moments of a number of styrene derivatives have been determined together with those of several analogous compounds with saturated side chains attached to the benzene ring. These moments have been discussed in terms of the more important electromeric forms of these molecules.

NOTRE DAME, INDIANA RECEIVED JANUARY 28, 1938

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(5) *Org. Syntheses*, **9**, 66 (1929).

(6) *Ibid.*, **5**, 27 (1925).

(7) Smyth and Rogers, THIS JOURNAL, **52**, 2227 (1930).