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

The Dielectric Properties of Acetylenic Compounds. III. Substituted Phenylacetylenes

BY M. M. OTTO AND H. H. WENZKE

A value of 0.66 *D* has been reported by Bergmann and Tschudnowsky[1] for the moment of phenylacetylene. This value is high because it was calculated from polarizations made in solution at one temperature with the consequent neglect of atomic polarization. *p*-Nitrophenylacetylene has a moment of 3.63 *D*[1] and if compared with the moment of nitrobenzene, which is 3.98 *D*, this would indicate a moment of 0.35 for the phenylacetylene group. The data on *p*-nitrophenylacetylene indicate that the moment of phenylacetylene is opposite in direction from that of toluene. In order to establish more definitely the direction and magnitude of the moment of phenylacetylene, data were obtained on a number of ortho, meta and para substituted phenylacetylenes. It was also thought advisable to repeat the work on *p*-nitrophenylacetylene as a value of 3.63 seems too high.

Experimental Part

All dielectric constants were obtained by a modified heterodyne beat method previously described[2] using a radio broadcasting station (WGN) as a source of constant frequency oscillations. Densities were determined in a pycnometer of approximately 13 cc. capacity and the refractive index was measured with a Pulfrich refractometer. The details of preparing and identifying the compounds, some of which have not been reported before, are described in an article by Otto.[3]

The polarizations at infinite dilution were calculated by the method of Hedestrand.[4] In Table II are listed the values of the polarization at infinite dilution, the molecular refraction for the sodium line and the electric moment.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF SUBSTITUTED PHENYLACETYLENES

c_2	d	ϵ
	p-Chlorophenylacetylene	
0.03901	0.8844	2.332
.04290	.8855	2.341
.05608	.8898	2.362
.07116	.8943	2.386
.07808	.8965	2.395
.12420	.9116	2.463
	p-Bromophenylacetylene	
0.02485	0.8915	2.319
.03993	.9031	2.342
.04222	.9049	2.344
.07778	.9330	2.403
	m-Chlorophenylacetylene	
0.02443	0.8808	2.346
.03521	.8841	2.375
.04422	.8868	2.400
.06106	.8920	2.447
	o-Chlorophenylacetylene	
0.02392	0.8788	2.380
.03408	.8825	2.422
.04605	.8863	2.471
.06650	.8935	2.558
.07385	.8958	2.589
	o-Bromophenylacetylene	
0.01751	0.8843	2.359
.01950	.8853	2.365
.02242	.8877	2.377
.02931	.8922	2.414
.04574	.9028	2.487
	p-Ethylphenylacetylene	
0.03477	0.8739	2.334
.04044	.8741	2.341
.04872	.8745	2.360
.05590	.8751	2.369
.06357	.8752	2.382
	p-Methylphenylacetylene	
0.02620	0.8744	2.318
.04000	.8750	2.338
.05255	.8757	2.355
.06201	.8762	2.371
.10260	.8783	2.424
.1549	.8810	2.501
.2360	.8849	2.597
	p-Isopropylphenylacetylene	
0.02869	0.8733	2.331
.03466	.8735	2.343
.06099	.8747	2.387
.09569	.8766	2.455
	p-Nitrophenylacetylene	
0.005909	0.87471	2.3750
.007581	.87556	2.4056
.011181	.87704	2.4651
.012662	.87788	2.4918

---

[1] Bergmann and Tschudnowsky, *Z. physik. Chem.*, **B17**, 1116 (1932).

[2] Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **6**, 187 (1934).

[3] Otto, THIS JOURNAL, **56**, 1393 (1934).

[4] Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

TABLE II

POLARIZATIONS AND MOMENTS OF SUBSTITUTED PHENYLACETYLENES

Phenylacetylene	P_∞	MR_D	$10^{18}\mu$
p-Chloro-	58.85	39.71	0.96
p-Bromo-	61.26	42.61	.95
m-Chloro-	78.46	39.11	1.38
m-Bromo-	80.79	43.18	1.35
o-Chloro-	99.53	39.76	1.69
o-Bromo-	109.15	42.66	1.79
p-Ethyl-	67.47	44.62	1.05
p-Methyl-	60.09	39.14	1.01
p-Isopropyl-	75.24	49.23	1.12
p-Nitro-	286.7	45.00[a]	3.42

[a] Taken from Bergmann and Tschudnowsky, Ref. 1.

Discussion of Results

The paraffin hydrocarbons like methane and ethane have no moment. This is also true of benzene. If however a phenyl group is substituted for a hydrogen atom of methane the compound formed, toluene, has a moment of 0.4 *D*. From the moments of the various derivatives of toluene it has been shown that the plus end of the toluene moment is toward the methyl group. An inspection of the values of Table II will show that the moment of the phenylacetylene is in a direction opposite to that in toluene. By taking the values of the moments of chlorobenzene, bromobenzene, toluene and nitrobenzene as 1.52, 1.50, 0.40 and 3.98, respectively, the moments of the para-substituted phenylacetylenes give values of 0.56, 0.55, 0.61 and 0.56 for the moment of phenylacetylene. The error in neglecting P_A is smallest with *p*-nitrophenylacetylene and 0.56 will be accepted as the best value for the phenylacetylene moment. Using a value of 0.56 for the phenylacetylene moment, the moments of the meta-substituted phenylacetylenes can be calculated. For *m*-chlorophenylacetylene the calculated moment is 1.34 as compared to an observed value of 1.38. For *m*-bromophenylacetylene the calculated moment is 1.31 and the observed 1.35. No numerical calculations were attempted with the ortho substituted compounds as usually the results are erroneous because owing to the close proximity of the groups inductive effects are very prominent. In spite of the "ortho effect" the moments of the ortho substituted phenylacetylenes are considerably greater than those of the meta compounds. This is of course as expected.

Summary

1. The replacement of a hydrogen of acetylene with a phenyl group causes a redistribution of electricity such that the compound has a moment of approximately 0.56 *D*.
2. This moment is opposite in direction to that present in toluene.
3. Electric moments have been determined for *p*-chloro-, *p*-bromo-, *m*-chloro-, *m*-bromo-, *o*-chloro-, *o*-bromo-, *p*-methyl-, *p*-ethyl-, *p*-isopropyl-, and *p*-nitrophenylacetylenes.

NOTRE DAME, INDIANA RECEIVED APRIL 5, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Catalytic Decomposition of Hydrogen Peroxide in an Acid Chlorine–Chloride Solution. II. The Steady State Function at 0 to 25°

BY BENJAMIN MAKOWER

Introduction

The catalytic decomposition of hydrogen peroxide in the presence of chlorine and hydrogen chloride has been shown by Livingston and Bray[1] to be closely related to the two chemical reactions

$$H_2O_2 + 2H^+ + 2Cl^- = Cl_2 + 2H_2O \qquad (1)$$

$$H_2O_2 + Cl_2 = O_2 + 2H^+ + 2Cl^- \qquad (2)$$

and is believed to be due to the occurrence of these two compensating reactions at equal rates. In any given experiment, a steady state is established in which the concentrations of Cl_2, H^+ and Cl^- remain constant and the net result is

$$2H_2O_2 = O_2 + 2H_2O \qquad (3)$$

At the steady state, the concentration relations and the rate of disappearance of H_2O_2 were found by Livingston and Bray[1] to be governed by the equations

$$R = (Cl_2)/(H^+)^2(Cl^-)^2 \qquad (4)$$

and

$$d(H_2O_2)/dt = k(H_2O_2)(H^+)(Cl^-) \qquad (5)$$

These results, and the analogy to the corresponding bromine system studied previously by Bray and Livingston[2] led to the following interpretation.

---

[1] Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925).

[2] Bray and Livingston, *ibid.*, **45**, 1251 (1923).