

1D oxygen atom approaching a hydrogen molecule. A normal atom requires more activation (about 8 kg. cal.) and also has a barrier of high curvature at the maximum. Such barriers of very high curvature, which can arise with a change in multiplicity, may well be effective in the separation of isotopes by the tunnel effect. There is also an additional slowness of reaction resulting from transition between states of different multiplicities.

These results are in satisfactory agreement with the known experimental facts. Kistiakowsky¹⁶ and Harteck and Kopsch¹⁷ have studied this reaction. The results of the former seem to indicate that an excited 1D atom will need a small activation, while a normal atom will require more. Actual temperature dependence of the reaction was used by Harteck and Kopsch to show an activation energy of 6 kg. cal. for the normal-atom reaction.

In the above calculation the activated state for the singlet system came at values of r_1 at which the ionic interactions had vanished. These results indicate that in reactions which convert

(16) Kistiakowsky, *THIS JOURNAL*, **52**, 1868 (1930).

(17) Harteck and Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

polar into non-polar compounds, or *vice versa*, the activated state may occur at distances for which the polar forces are relatively unimportant. This rapid disappearance of the polar part of the bond is associated with the customary high ionization potential of atoms and molecules, which makes the polar level lie high above the homopolar one at activated state configurations. Most ionic reactions are rapid, though in solutions hydration effects are a complication and in oxidation-reduction reactions involving the approach of highly charged ions of like signs reaction is sometimes slow.

A completely satisfactory treatment of the problems here discussed must await the further development of the quantum mechanical variation method. In the meantime the use of all available experimental information, together with the perturbation theory, provides a less satisfying but apparently essentially correct picture of such reactions. It is hoped that the information provided by this study of the H_2O molecule will facilitate consideration of similar but more complicated systems.

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RECEIVED JUNE 23, 1934

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The Dielectric Properties of Acetylenic Compounds. IV. Arylhalogenoacetylenes. Positive Iodine

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It has been shown by Pflaum and Wenzke¹ that there is a considerable reduction in the carbon to halogen moment in the alkyl halogenoacetylenes as compared to halogen derivatives of the paraffins, benzene and ethylenic compounds. The chemical behavior of the halogens attached to an acetylenic carbon indicates that they are "positive" in character. It would perhaps be more correct to say that chemical evidence indicates that the halogen atoms when attached to an acetylenic carbon are not as highly negative as when linked to more saturated carbon atoms. It is not the purpose of this article to discuss the chemical evidence that has been presented by various investigators. The electric moment data on arylhalogenoacetylenes should prove to be even of more interest than that on the alkylhalogenoacetylenes. This is true partly because

(1) Pflaum and Wenzke, *THIS JOURNAL*, **56**, 1106 (1934).

the treatment of moments as vector quantities is more satisfactory in aryl derivatives on account of the rigidity of the structure of the benzene molecule. By the selection of appropriate derivatives one can then obtain more nearly quantitative data on the acetylenic carbon to halogen moment in aryl compounds than is possible in alkyl compounds. Chemical evidence also indicates that the halogens in the aryl acetylenic derivatives is even more "positive" than in the alkyl compounds.

Preparation of Compounds

All of the iodoacetylenes were made by the method of Vaughn and Nieuwland,² which is that of direct iodination in liquid ammonia as a solvent. Phenyl and tolyl iodoacetylenes were purified by repeated crystallization from the solvent heptane. In order to reduce the solubility the heptane was cooled by liquid ammonia. *p*-Chloro-

(2) Vaughn and Nieuwland, *ibid.*, **55**, 2150 (1933).

phenyliodoacetylene, *o*-chlorophenyliodoacetylene and *p*-nitrophenyliodoacetylene were purified to a constant melting point by crystallization from alcohol.

The bromoacetylenes were prepared³ by stirring the acetylenes in an aqueous solution of sodium hypobromite for three or four hours. Phenylbromoacetylene and *p*-tolylbromoacetylene were purified by distillation under reduced pressure. *p*-Nitrophenylbromoacetylene was purified by repeated crystallization of the pure substance.

The substituted chloro- and nitrophenylacetylenes were prepared from the corresponding benzaldehydes by forming the cinnamic acids by the Perkin synthesis, esterifying (either methyl or ethyl), and brominating by the direct addition of bromine with stirring. Then the substituted ethyl α,β -dibromocinnamates were treated with alcoholic potassium hydroxide, giving the potassium salt of the substituted phenylpropionic acids. To the aqueous solution of the potassium salts was added an excess of cupric nitrate and the substituted phenylacetylenes then steam distilled.

Phenylchloroacetylene and *p*-tolylchloroacetylene were prepared by suspending the sodium salt in dry ether and adding benzene sulfonyl chloride.⁴

TABLE I

Acetylene	M. p., °C.	B. p., °C.
Phenyliodo-	9	
<i>p</i> -Tolyliodo-	39	
<i>p</i> -Chlorophenyliodo-	114	
<i>o</i> -Chlorophenyliodo-	106	
<i>p</i> -Nitrophenyliodo-	182	
Phenylbromo-		84-85 at 10 mm.
<i>p</i> -Tolylbromo-		92-93 at 10 mm.
<i>p</i> -Nitrophenylbromo-	167	
Phenylchloro-		74 at 18 mm.
<i>p</i> -Tolylchloro		88-89 at 30 mm.

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF ARYLHALOGENOACETYLENES (Solvent, benzene; temp., 25°)

ϵ_2	ϵ	d
Phenyliodoacetylene		
0.082824	2.3594	0.97158
.068731	2.3417	.95487
.048267	2.3200	.92587
.000000	2.2760	.87215
Phenylbromoacetylene		
0.10679	2.4247	0.95586
.08011	2.3852	.93506
.04209	2.3320	.90564
.00000	2.2760	.87238
Phenylchloroacetylene		
0.10290	2.4792	0.90300
.061854	2.3973	.89118
.033074	2.3408	.88251
.000000	2.2760	.87238

(3) Straus, Kollek and Heyn, *Ber.*, **63**, 1880 (1930).

(4) Truchet, *Ann. chim.*, **16**, 309 (1931).

<i>p</i> -Tolyliodoacetylene		
0.099556	2.4594	0.99123
.080091	2.4240	.96930
.050310	2.3708	.93430
.000000	2.2760	.87215
<i>p</i> -Tolylbromoacetylene		
0.12192	2.5692	0.94810
.082394	2.4751	.92422
.051341	2.3991	.90368
.000000	2.2760	.87185
<i>p</i> -Tolylchloroacetylene		
0.072537	2.6489	0.88571
.055256	2.5626	.88246
.043530	2.5000	.88021
.000000	2.2760	.87185
<i>p</i> -Chlorophenyliodoacetylene		
0.047592	2.3901	0.94530
.027056	2.3425	.91491
.016584	2.3153	.89767
.000000	2.2760	.87215
<i>o</i> -Chlorophenyliodoacetylene		
0.08282	2.5715	0.99964
.05655	2.4779	.95782
.04415	2.4380	.93821
.02721	2.3788	.91443
.00000	2.2760	.87213
<i>p</i> -Nitrophenyliodoacetylene		
0.006618	2.4163	0.88304
.004075	2.3619	.87874
.002982	2.3411	.87703
.000000	2.2760	.87238
<i>p</i> -Nitrophenylbromoacetylene		
0.010997	2.4484	0.88515
.0062129	2.3749	.87966
.0036654	2.3344	.87662
.0000000	2.2760	.87238

The polarizations at infinite dilution were determined from the slopes of the dielectric constant and density curves at zero concentration.

TABLE III

POLARIZATIONS OF ARYLHALOGENOACETYLENES

Acetylene	P_∞	MR _D	$P_A + M$
Phenyliodo-	55.69	49.33	6.36
Phenylbromo-	58.20	43.21	14.99
Phenylchloro-	66.27	41.01	25.26
<i>p</i> -Tolyliodo-	72.87	53.46	19.41
<i>p</i> -Tolylbromo-	82.85	49.48	33.37
<i>p</i> -Tolylchloro-	121.40	46.45	74.95
<i>p</i> -Chlorophenyliodo-	77.53	54.44	23.09
<i>o</i> -Chlorophenyliodo-	96.79	54.88	41.91
<i>p</i> -Nitrophenyliodo-	357.0	57.8	299.2
<i>p</i> -Nitrophenylbromo-	273.8	52.8	221.0

An examination of the data of Table IV shows that in each case the carbon to iodine moment is more positive than the carbon to hydrogen

TABLE IV
MOMENTS OF ARYLHALOGENOACETYLENES AND THE
CORRESPONDING ACETYLENES⁵

	10 ¹⁸ μ
Phenylacetylene	0.66
Phenyliodoacetylene	.55
Phenylbromoacetylene	.85
Phenylchloroacetylene	1.10
<i>p</i> -Methylphenylacetylene	1.01
<i>p</i> -Tolyliodoacetylene	0.97
<i>p</i> -Tolylbromoacetylene	1.27
<i>p</i> -Tolylchloroacetylene	1.90
<i>p</i> -Chlorophenylacetylene	0.96
<i>p</i> -Chlorophenyliodoacetylene	1.06
<i>o</i> -Chlorophenylacetylene	1.69
<i>o</i> -Chlorophenyliodoacetylene	1.42
<i>p</i> -Nitrophenylacetylene	3.42
<i>p</i> -Nitrophenyliodoacetylene	3.80
<i>p</i> -Nitrophenylbromoacetylene	3.27

moment in the corresponding acetylene. In the cases of phenylacetylene and tolylacetylene the plus end of the moment is away from the acetylene grouping, and the moment of the iodo derivatives is smaller. With *p*-chlorophenylacetylene and *p*-nitrophenylacetylene the negative end of the moment is toward the benzene ring and the iodo derivatives have larger moments than the parent compounds. It is also to be noted that *o*-chlorophenyliodoacetylene has a smaller moment than *o*-chlorophenylacetylene. This also indicates that the carbon to iodine moment is more positive than the corresponding carbon to hydrogen moment. As all of the data were taken in solutions at constant temperature it was of course necessary to neglect atomic polarization in the calculations. This factor, however, in no way affects the validity of the conclusions although it would render inaccurate a quantitative comparison of the carbon to hydrogen with carbon to iodine moments. As the hydrogen is undoubtedly more positive than the carbon to which it is at-

(5) The data on the substituted phenylacetylenes are taken from Otto and Wenzke, *THIS JOURNAL*, **56**, 1314 (1934).

tached, it seems correct to apply the term "positive iodine" to the iodine atom in the aryliodoacetylenes.

The carbon to bromine moment and the carbon to chlorine moment are much less negative in the acetylenic compounds than in the more saturated compounds such as the benzene derivatives. The carbon to bromine moment in *p*-nitrophenylbromoacetylene is 0.15 more negative than the acetylenic carbon to hydrogen moment. The moment of bromobenzene is 1.50, which means of course that the carbon to bromine moment is 1.50 more negative than the carbon to hydrogen moment in benzene. Using the data of *p*-tolylchloroacetylene it will be seen that the carbon to chlorine moment is 0.89 more negative than the acetylenic carbon to hydrogen moment. The moment of chlorobenzene is 1.52. Dipole moments thus give evidence by direct physical measurement of the much less negative character of the carbon to chlorine and the carbon to bromine moments in the substituted acetylenic compounds.

Summary

1. The dipole moments of a number of arylhalogenoacetylenes have been measured.
2. It has been shown that the carbon to iodine moment in aryliodoacetylenes has the plus end toward the iodine atom.
3. It has been shown that the carbon to bromine moment and the carbon to chlorine moment in arylhalogenoacetylenes is less than the corresponding carbon to halogen moments in substituted benzenes. The bromine and chlorine are "negative" but much less so than in the more saturated derivatives such as those of the paraffins, ethylenes and benzenes.
4. The conclusions reached by electric moment measurements are in agreement with those reached by less direct chemical evidence.

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RECEIVED JUNE 26, 1934